

Supporting Information

Determination of the evolution of heterogeneous single metal atoms and nanoclusters under reaction conditions: which are the working catalytic sites?

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Experiments

1. Synthesis of different types of Pt species on various supports

TiO₂ (nanopowder, from Sigma-Aldrich, product No. 718467-100G), Al₂O₃ (from NanoScale NanoActive®, with a surface area of ~300 m²/g) and nanosized CeO₂ (from Rhodia with a surface area of ~120 m²/g) were used as the support to prepare supported Pt catalysts, by conventional wet impregnation.

1.1 Synthesis of Pt/TiO₂ with H₂PtCl₆ as the precursor

2 g of TiO₂ support was dispersed in 50 mL aqueous solution of H₂PtCl₆ (containing certain amount of Pt, determined by the loading of Pt in the final catalyst) under rigorous stirring. After 2 h of stirring at room temperature, water was removed by rotavapor. The obtained solid was dried at 100 °C overnight and then calcined in flow air at 400 °C for 2 h with a ramp of 2 °C/min, resulting the formation of singly dispersed Pt atoms on TiO₂ when the Pt loading is ~0.03 wt%. Supported Pt catalysts with clusters and nanoparticles were prepared by reducing the Pt/TiO₂ catalysts at 450 °C by H₂. The size of Pt particles depends on the Pt loading. The final Pt loadings in various samples were determined by ICP analysis.

1.2 Synthesis of Pt/TiO₂ with platinum(II) acetylacetonate as the precursor

0.5 g of TiO₂ support was dispersed in 40 mL ethanol solution of platinum(II) acetylacetonate under rigorous stirring. After 2 h of stirring at room temperature, water was removed by rotavapor. The obtained solid was dried at 60 °C overnight and then calcined in flow air at 350 °C for 2 h with a ramp of 1 °C/min, resulting the formation of singly dispersed Pt atoms on TiO₂ when the Pt loading is ~0.04 wt%. Supported Pt catalysts containing Pt clusters and nanoparticles were prepared by reducing the Pt/TiO₂ catalysts at 450 °C by H₂. The size of Pt particles supported on TiO₂ depends on the Pt loading. The final Pt loadings in various samples were determined by ICP analysis.

1.3 Synthesis of PtNP/TiO₂ samples by loading colloid Pt nanoparticles on TiO₂

Colloid Pt nanoparticles were synthesized by heating the ethanol solution containing H₂PtCl₆ in the presence of polyvinylpyrrolidone (PVP, K55). In a typical procedure, 16.6 mg of PVP, 45 mL ethanol and 5.0 mL of H₂PtCl₆ solution (6.0 mmol/L) was mixed at room temperature. The solution

was then kept under reflux at 90 °C for 3 h. The color of the solution would turn from light yellow to grey after 3 h, indicating the formation of colloid Pt nanoparticles in ethanol. 3.0 g of TiO₂ powder was then added to the ethanol solution and kept stirring for 2 h. The ethanol solvent was removed by heating the solution at 90 °C in oil bath. Afterwards, the solid sample was subjected to calcination in air at 400 °C for 2 h with a ramp rate of 2 °C/min, giving to the PtNP/TiO₂-air sample. The PtNP/TiO₂-450H₂ was obtained by reducing the PtNP/TiO₂-air sample by H₂ at 450 °C for 3 h. The final Pt loading was 0.2 wt%, determined by ICP analysis.

1.4 Synthesis of Pt/Al₂O₃ samples

2 g of Al₂O₃ support was dispersed in 50 mL aqueous solution of H₂PtCl₆ (containing certain amount of Pt, determined by the loading of Pt in the final catalyst) under rigorous stirring. After 2 h of stirring at room temperature, water was removed by rotavapor. The obtained solid was dried at 100 °C overnight and then calcined in flow air at 450 °C for 3 h with a ramp of 1 °C/min, resulting the formation of singly dispersed Pt atoms on Al₂O₃. Supported Pt catalysts with clusters and nanoparticles were prepared by reducing the Pt/ Al₂O₃ catalysts at 450 °C by H₂. The loading of Pt/Al₂O₃ was 0.2 wt%, determined by ICP.

To reduce the single Pt atoms supported on Al₂O₃ under mild conditions, the Pt/Al₂O₃-SA sample was mixed with NaBH₄ or hydrazine aqueous solution at 50 °C for 2 h. After the reduction treatment, the solid sample was isolated by centrifugation and then used for catalytic hydrogenation reaction.

1.5 Synthesis of Pt/CeO₂ samples

2 g of CeO₂ support was dispersed in 50 mL aqueous solution of H₂PtCl₆ (containing certain amount of Pt, determined by the loading of Pt in the final catalyst) under rigorous stirring. After 2 h of stirring at room temperature, water was removed by rotavapor. The obtained solid was dried at 100 °C overnight and then calcined in flow air at 450 °C for 3 h with a ramp of 1 °C/min, resulting the formation of singly dispersed Pt atoms on CeO₂. Supported Pt catalysts with clusters and nanoparticles were prepared by reducing the Pt/CeO₂ catalysts at 500 °C by H₂. The loading of Pt/CeO₂ was 0.2 wt%, determined by ICP.

2. Characterization on the Pt catalysts

Samples for electron microscopy studies were prepared by dropping the suspension of the powder

catalyst using ethanol as the solvent directly onto holey-carbon coated Cu grids. The measurements were performed in a JEOL 2100F microscope operating at 200 kV both in transmission (TEM) and scanning-transmission modes (STEM). STEM images were obtained using a High Angle Annular Dark Field detector (HAADF), which allows Z-contrast imaging. High-resolution STEM measurement was performed on FET Titan low-base microscope at 300 kV equipped with a Cs probe corrector, a monochromator and an ultrabright X-FEG electron source. The convergence angle was 25 mrad and the inner and outer angles for HAADF imaging were 70 and 200 mrad, respectively.

Hydrogen /deuterium (H/D) exchange experiments were carried out in a flow reactor at 25 and 80 °C. The feed gas consisted of 4 mL/min H₂, 4 mL/min D₂ and 18 mL/min argon, and the total weight of catalyst was ~7 mg. Reaction products (H₂, HD and D₂) were analysed with a mass spectrometer (Omnistar, Balzers). For the 0.03Pt/TiO₂-SA sample, it was measured after activation in N₂ at 150 °C. For 0.03Pt/TiO₂-450H₂ and 0.2Pt/TiO₂-450H₂ samples, they were reduced by H₂ at 200 °C in the reactor before the H/D exchange experiments. After the activation process, the temperature was decreased to 25 °C and, once stabilized, the H₂ feed was change to the reactant gas composition.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption Fine Structure (EXAFS) at Pt L₃-edge (11564 eV) of Pt/Al₂O₃ samples were measured at 20-BM-B of the Advanced Photon Source at Argonne National Laboratory. A Si (111) fixed-exit, double-crystal monochromator was used and 0.5 eV energy resolution. Harmonic rejection was facilitated using a Rh-coated mirror (4mrad) as well as a 15% detuning of the beam intensity at ~1000 eV above the edge of interest. Data was collected in fluorescence mode using a four elements Vortex Si Drift detector. Details on the beamline optics and instruments can be found elsewhere.¹ The samples were prepared as pellets and placed in a furnace with Kapton® windows.² For the Pt/TiO₂ sample, XAS data of Pt L₃-edge was collected using an unfocused beam at 20-ID-C beamline at the APS. Both measurements were performed in fluorescence mode using a four elements Vortex Si Drift detector. Details on the beamline optics and instruments can be found elsewhere (Heald, 2011, Heald, Cross, Brew, & Gordon, 2007). The samples were prepared as pellets and placed in a furnace with Kapton® windows (Kropf et al., 2013).

The EXAFS of three as-received Pt/Al₂O₃ samples were measured directly at room temperature without any pre-treatments, to study the chemical states and coordination environment of Pt species

after having contact with air. In order to follow the agglomeration of single Pt atoms into Pt clusters during the H₂ reduction treatment, the Pt/Al₂O₃-SA sample was reduced by a H₂/He flow of 100 mL/min (H₂:He = 3.5:1) at 200 °C for 30 min, corresponding to the Pt/Al₂O₃-200H₂. XANES spectra were recorded during the heating. After the reduction treatment, the sample was cooled down to room temperature in H₂ flow and EXAFS spectra were recorded ($k_{\text{max}} = 13 \text{ \AA}^{-1}$). Similarly, the Pt/Al₂O₃-SA sample was reduced under the same conditions but up to 450 °C, corresponding to the Pt/Al₂O₃-450H₂ sample. After the reduction treatment at 450 °C, the following measurements were performed in the same way as for Pt/Al₂O₃-200H₂ sample. For the *in situ* XAS experiments under CO+O₂ reaction conditions, the samples were exposed to the feed gas (CO:O₂ = 2:1, 100 mL min⁻¹) and then heated up to 225 °C with a ramp rate of 5 °C min⁻¹. The sample was kept at 225 °C for 1 h. Then, the temperature was further increased to 325 °C with a ramp rate of 5 °C min⁻¹, and then maintained at 325 °C for 2 h. XANES spectra were recorded during the heating and EXAFS was measured at 225 °C and 325 °C ($k_{\text{max}} = 13 \text{ \AA}^{-1}$) in the presence of CO and O₂.

The as-received 0.2Pt/TiO₂-450H₂ sample was measured directly by EXAFS directly without any pre-treatment. Then, the 0.2Pt/TiO₂-450H₂ sample was reduced in situ under 30 mL/min (3.5% of H₂ in He). The temperature was increased to 50 °C (5 °C/min) for 1h. After that, the temperature was decreased to room temperature and 6 EXAFS spectra were recorded and averaged ($k_{\text{max}} = 12 \text{ \AA}^{-1}$). To avoid beam damage between each EXAFS measurement the sample position was shifted by 500 microns. Then, the same procedure was repeated but the reduction temperature increased to 200 °C and 450 °C.

EXAFS oscillations were extracted using Athena code and analysed using Artemis software.³ The local environment of the Pt atoms in the Pt/Al₂O₃ samples was determined using the phase shift and amplitude functions of Pt-O, Pt-Al and Pt-Pt contributions. These contributions were calculated using PtO₂, and Pt^o structures. For the Pt-Al contribution, we used the PtO structure and replaced in the FEFF file the oxygen in the second shell by an aluminum. In the case of Pt/TiO₂ sample, the local environment of the Pt atoms was determined using the phase shift and amplitude functions of Pt-O, Pt-Pt and Pt-Ti contributions. These contributions were calculated using PtO₂, Pt^o and PtTi structures. The photoelectron energy origin correction (ΔE_0) and the amplitude reduction factor (S_0^2) were found for the Pt foil and fixed for the samples. To decrease the number of parameters the Debye-Waller (σ_i^2)

was kept free but the same for all path, with exception of the second shell contribution in the Pt/Al₂O₃ fresh samples. In this case, it was fixed to 0.01. The coordination numbers (N_i) and distances (R_i) were adjusted freely and independently for each path and each sample. The range used to transform the EXAFS oscillations ($k^2 \chi(k)$) was 3-11 and the interval where the fit was performed (ΔR) was 1-3.

The FTIR spectra were collected with a Bruker “vertex 70” spectrometer equipped with a DTGS detector (4 cm⁻¹ resolution, 32 scans). An IR cell allowing in situ treatments in controlled atmospheres and temperatures from 25 °C to 500 °C has been connected to a vacuum system with gas dosing facility. Self-supporting pellets (ca. 10 mg cm⁻²) were prepared from the sample powders and treated in hydrogen flow (20 ml min⁻¹) at 400 °C for 1 h in the case of Pt/CeO₂-500H₂ samples and in N₂ at 100 °C for 1 h in the 0.2Pt/Al₂O₃-SA and 0.2Pt/CeO₂-SA samples. After activation, different experiments were performed. Thus, the 0.2Pt/Al₂O₃-SA sample was cooled down to 25°C and exposed to a CO+O₂ (1:2) flow (10 ml min⁻¹) at 25 °C. Then, the temperature is increased at a rate of 5 °C min⁻¹ to 225 °C and 325°C. IR spectra were collected at each temperature on the cooled down pellet. In the case of 0.2Pt/CeO₂-500H₂ and 0.2Pt/CeO₂-SA samples, after activation, they are cooled down and exposed to an O₂ flow (10 ml min⁻¹) for 1h at 25 °C and 80 °C. Spectra were collected at each temperature.

3. Catalytic studies on the Pt catalysts

3.1 Hydrogenation of 3-nitrostyrene

The hydrogenation of 3-nitrostyrene was performed in batch reactor. A certain amount of solid catalyst (10 mg or 20 mg), 0.5 mmol of 3-nitrostyrene, 50 µL of dodecane as internal standard, 2 mL of toluene as solvent was placed in the batch reactor. Then the reactor was purged with H₂ for several times. The reaction was performed at 40 or 50 °C with 3 bar of H₂. 50 µL of reaction mixture was taken out of the reactor at different reaction time and analyzed by GC with FID detector.

3.2 Hydrogenation of styrene

The hydrogenation of styrene was performed in batch reactor. A certain amount of solid Pt/Al₂O₃ catalyst (10 mg), 1.0 mmol of styrene, 50 µL of hexadecane as internal standard, 2 mL of toluene as solvent was placed in the batch reactor. Then the reactor was purged with H₂ for several times. The reaction was performed at 50 °C with 3 bar of H₂. 50 µL of reaction mixture was taken out of the reactor at different reaction time and analyzed by GC with FID detector.

3.3 CO oxidation with supported Pt catalysts

The CO oxidation was performed in a fix-bed reactor. 120 mg of solid Pt/oxide catalyst was used for each test. The feed gas was 2% of CO and 1% of O₂ balanced with He. The total flow was 85 mL/min. The product was analyzed by gas chromatograph with TCD detector.

3.4 Propane dehydrogenation reaction with Pt/Al₂O₃ catalysts

The reaction was performed with a fix-bed reactor under atmospheric pressure using N₂/propane as feed gas at 600 °C. The products were analyzed by a GC which can detect cracking products (methane, ethene and ethane), propylene, C₄, C₅ and aromatics. Before reaction, 140 mg of the solid catalyst was heated up N₂ flow (16 mL/min) with a ramp rate of 10 °C/min from room temperature up to 600 °C. After reaching 600 °C, the atmosphere was changed to reaction feed gas (5 mL/min of propane and 16 mL/min of N₂ as balanced gas) and the propane dehydrogenation started.

3.5 Photocatalytic H₂ evolution with Pt/TiO₂ catalysts

The photocatalyst powder (25 mg) was dispersed in a water/ethanol mixture (1:1 v/v, 25 mL) by sonication for 15 min. The resulting suspension was then transferred to a quartz cell (volume ≈ 50 mL, equipped with a gas inlet valve, a gas outlet valve and a pressure gauge) and purged with argon (5 mL/min for 10 min). Finally, the cell was pressurized with argon (1.5 bar) and tightly closed. The suspension was stirred at 500 rpm and irradiated with a medium pressure Hg lamp (125 W, irradiation intensity ≈ 1.5 kW/m²). The production of H₂ quantified by a GC with TCD detector.

References for the supporting information

1. Heald, S. M., Cross, J. O., Brewe, D. L., & Gordon, R. A. (2007). The PNC/XOR X-ray microprobe station at APS sector 20. *Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 582 (1), 215–217. <https://doi.org/10.1016/j.nima.2007.08.109>
2. Kropf, A. J., Wu, T., Lobo-Lapidus, R., Wang, H., Heald, S. M., Miller, J. T., ... Hu, Y. (2013). In situ intermediate-energy X-ray catalysis research at the advanced photon source beamline 9-BM. *Catalysis Today*, 205, 141–147. <https://doi.org/10.1016/j.cattod.2012.09.034>
3. Ravel, B., & Newville, M. (2005). ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation*, 12, 537–541. <https://doi.org/10.1107/S0909049505012719>

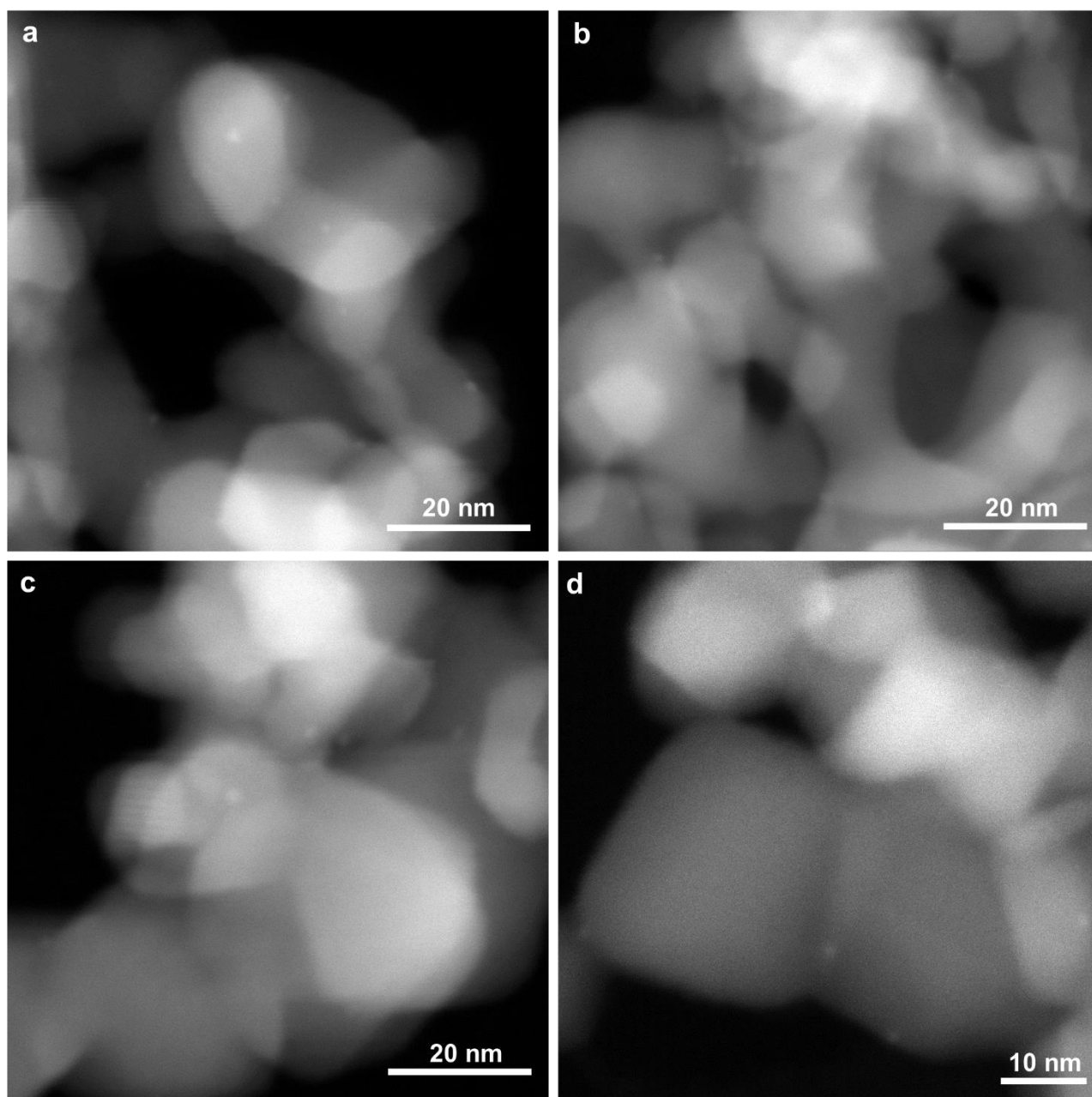


Figure S1. STEM images of 0.03Pt/TiO₂-450H₂, showing the presence of subnanometric Pt clusters supported on TiO₂.

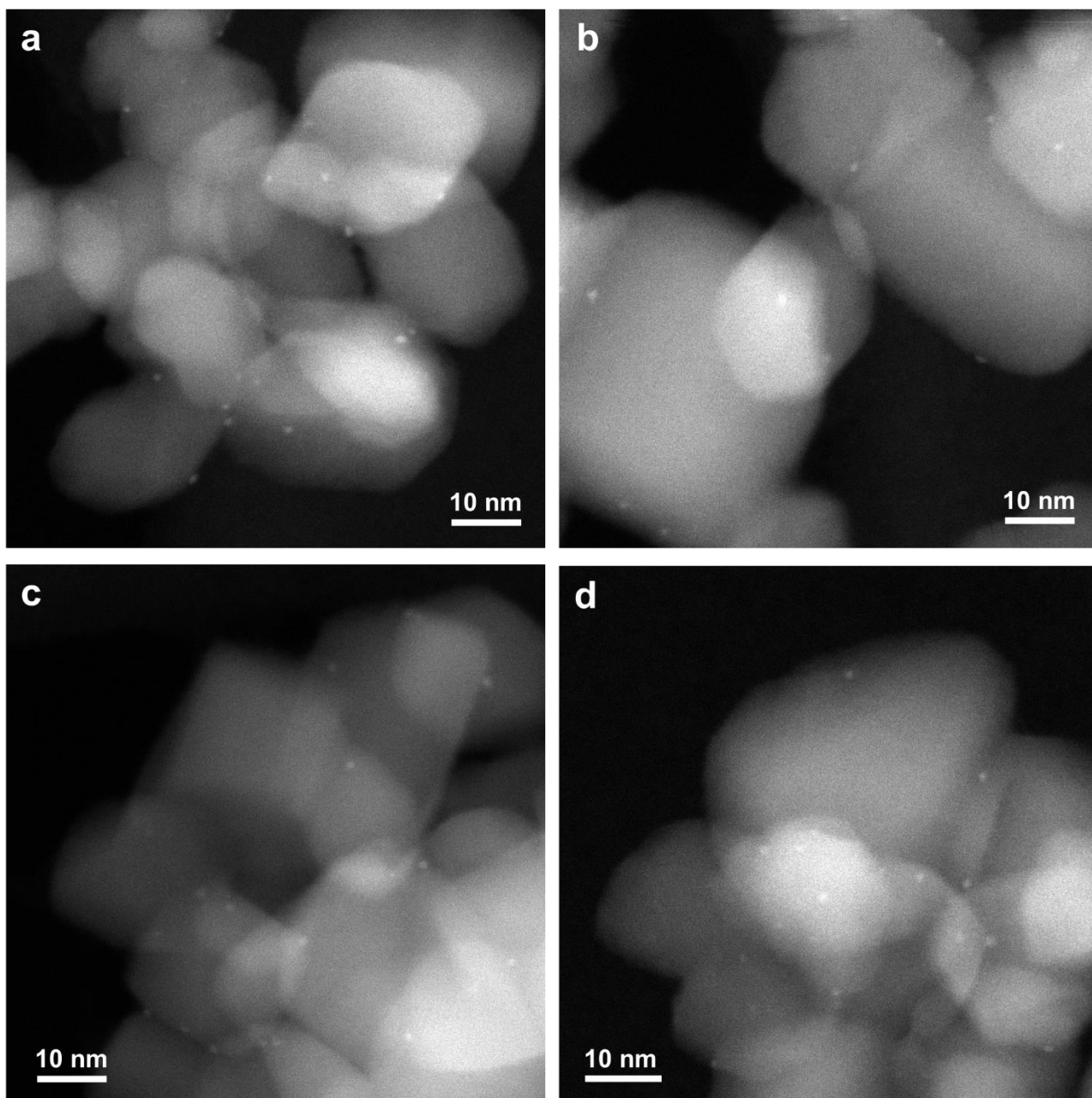


Figure S2. STEM images of 0.1Pt/TiO₂-450H₂, showing the presence of subnanometric Pt clusters supported on TiO₂.

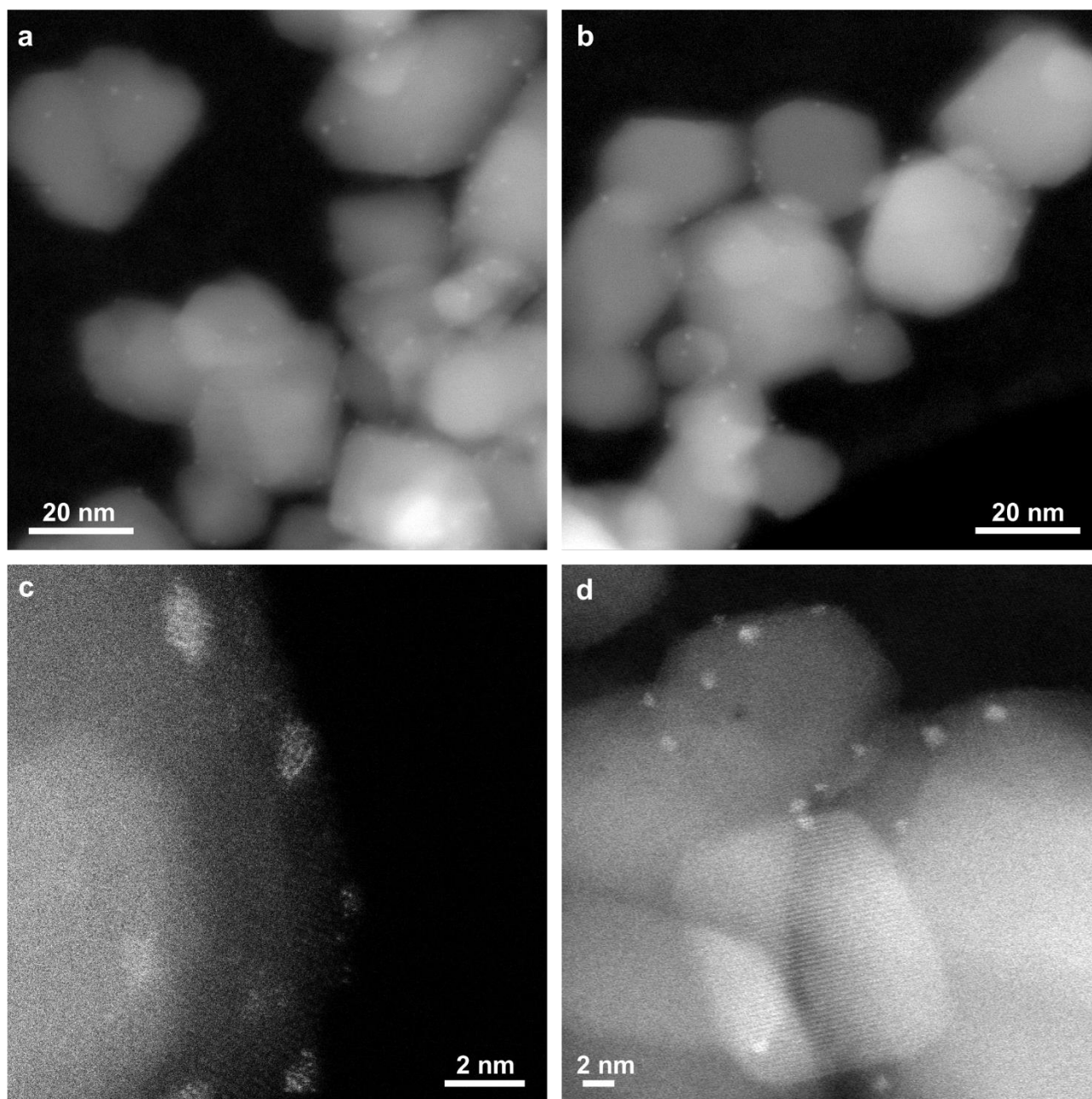


Figure S3. STEM images of 0.2Pt/TiO₂-450H₂, showing the presence of Pt nanoparticles supported on TiO₂.

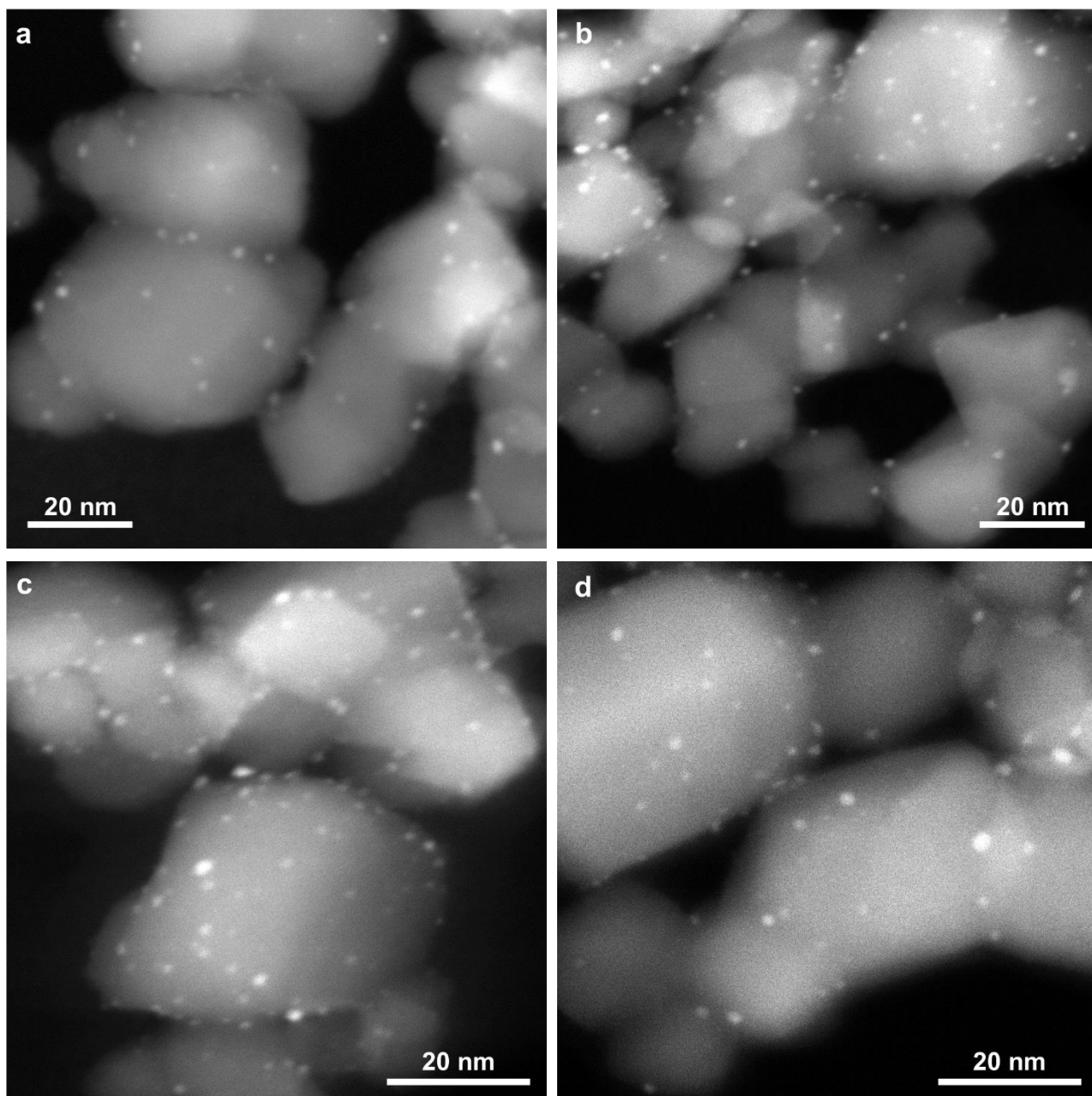


Figure S4. STEM images of 0.5Pt/TiO₂-450H₂, showing the presence of Pt nanoparticles supported on TiO₂.

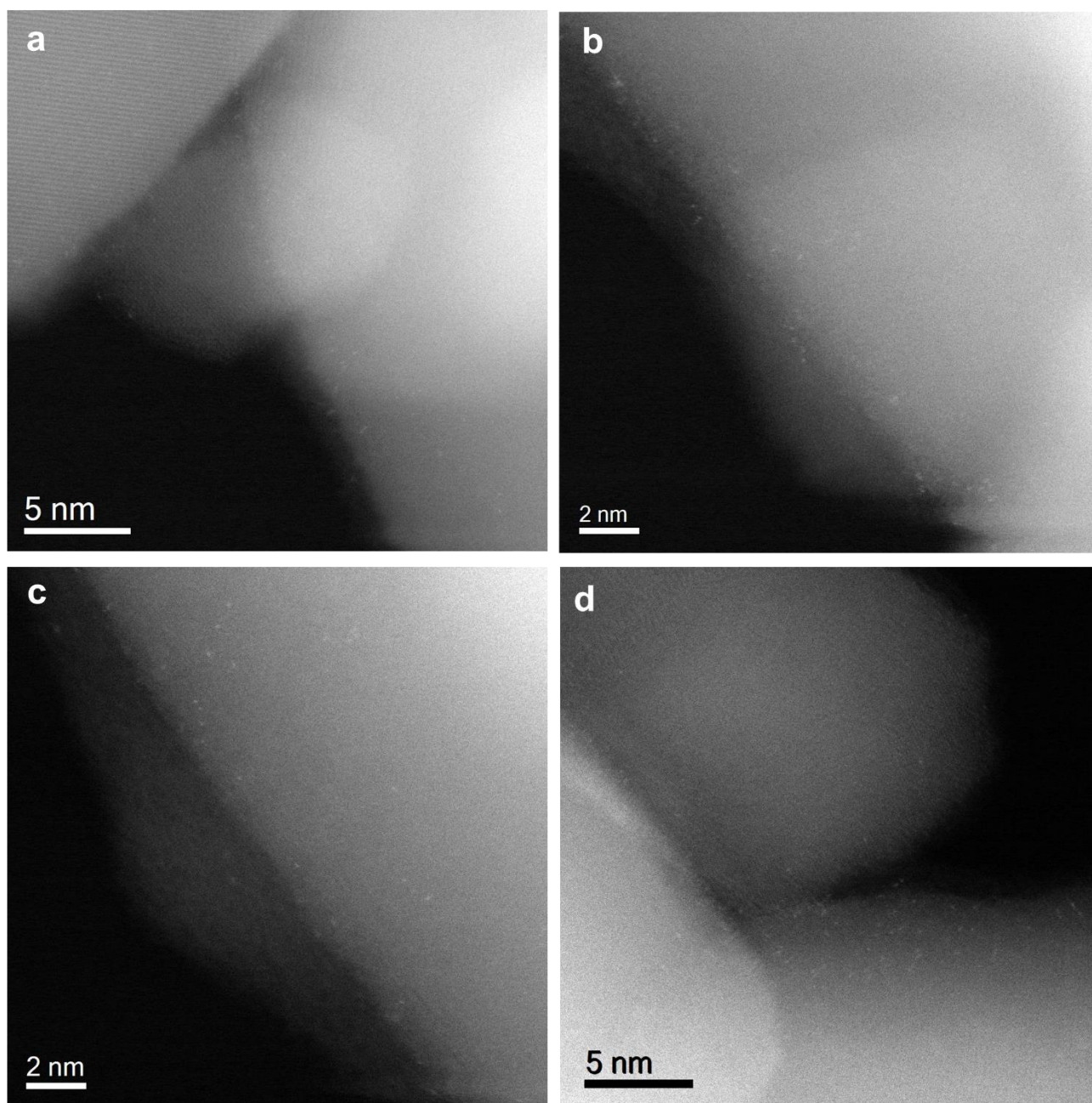


Figure S5. High-resolution STEM image of Pt/TiO₂-SA sample after the hydrogenation of 3-nitrostyrene reaction. These images confirm the stability of single Pt atoms under mild reaction conditions.

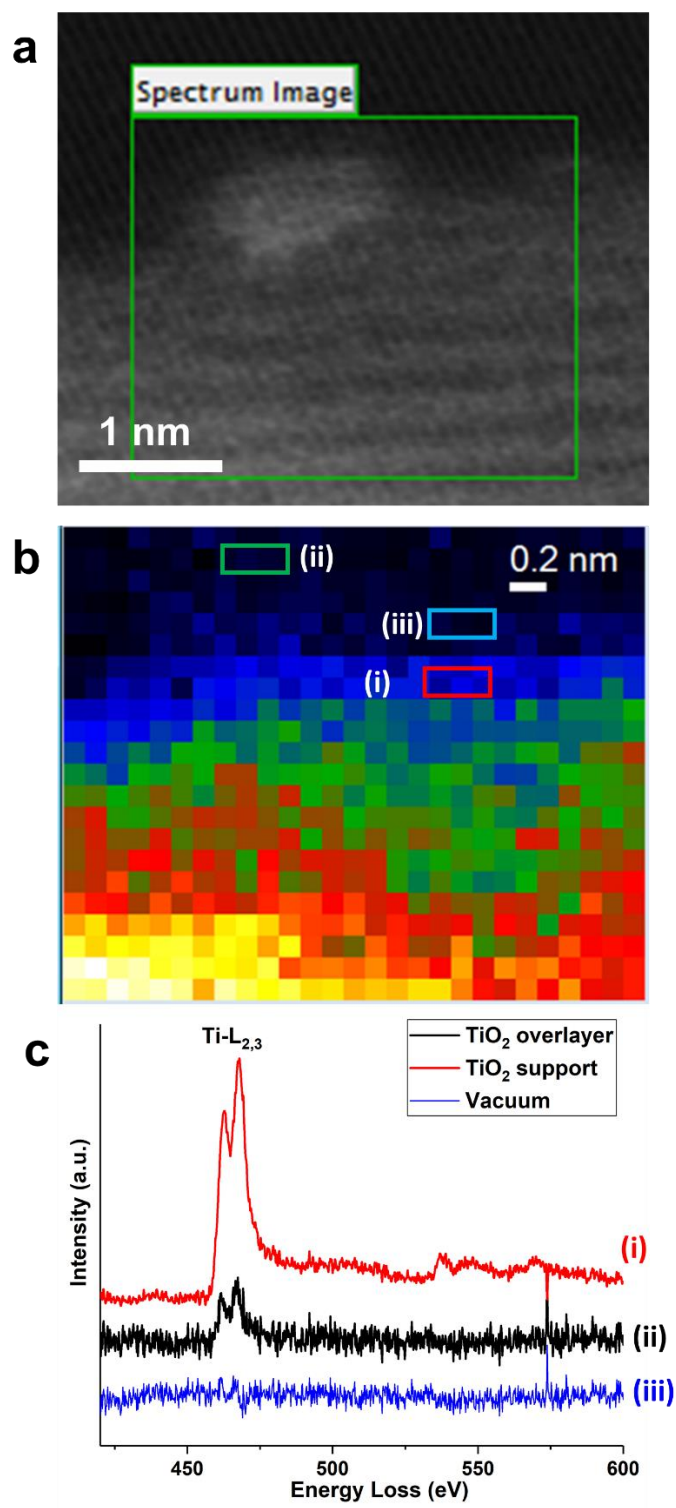


Figure S6. Atomic structure of 0.2Pt/TiO₂-450H₂ sample by high-resolution STEM and EELS spectroscopy. (a) A typical STEM image of Pt nanoparticle supported on TiO₂ with atomic resolution. (b) EELS mapping of the Ti-L edge in the selected area shown in (a). (c) Ti-L_{2,3} edge EELS spectra of three different areas shown in (b).

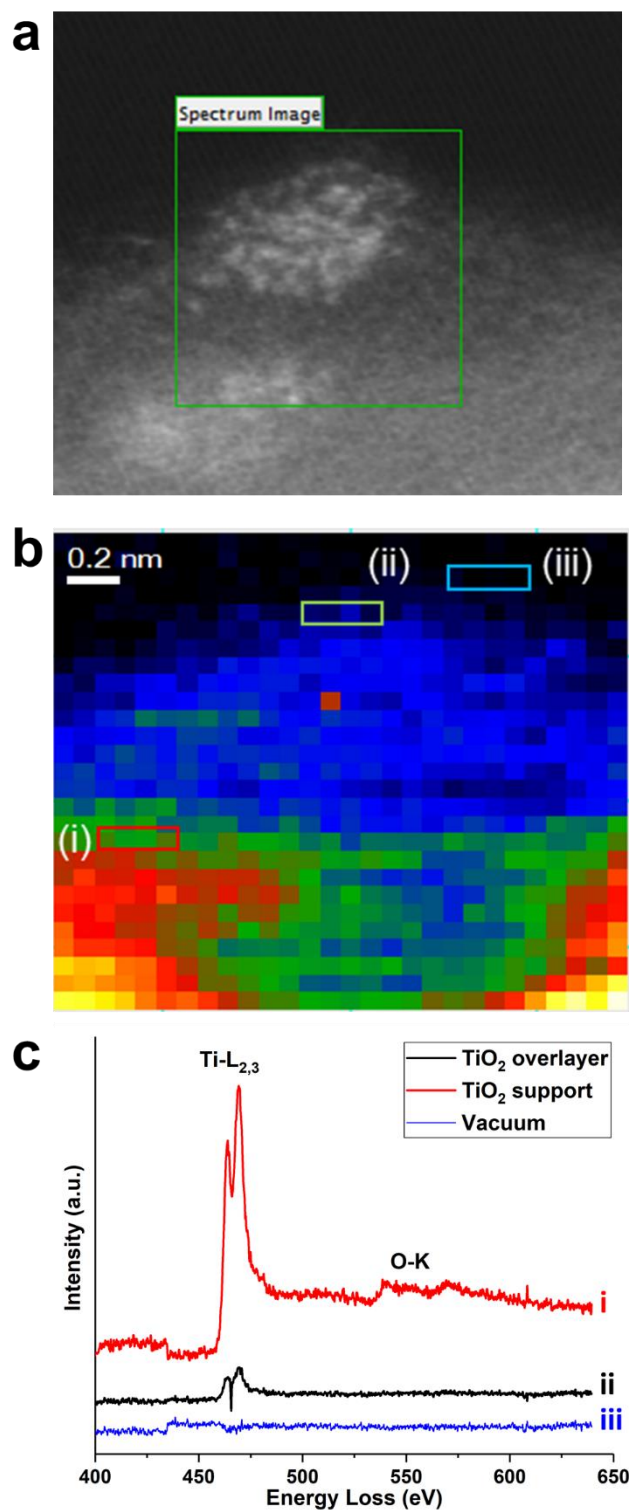


Figure S7. Atomic structure of 0.2Pt/TiO₂-450H₂ sample by high-resolution STEM and EELS spectroscopy. (a) A typical STEM image of Pt nanoparticle supported on TiO₂ with atomic resolution. (b) EELS mapping of the Ti-L edge in the selected area shown in (a). (c) Ti-L_{2,3} edge EELS spectra of three different areas shown in (b).

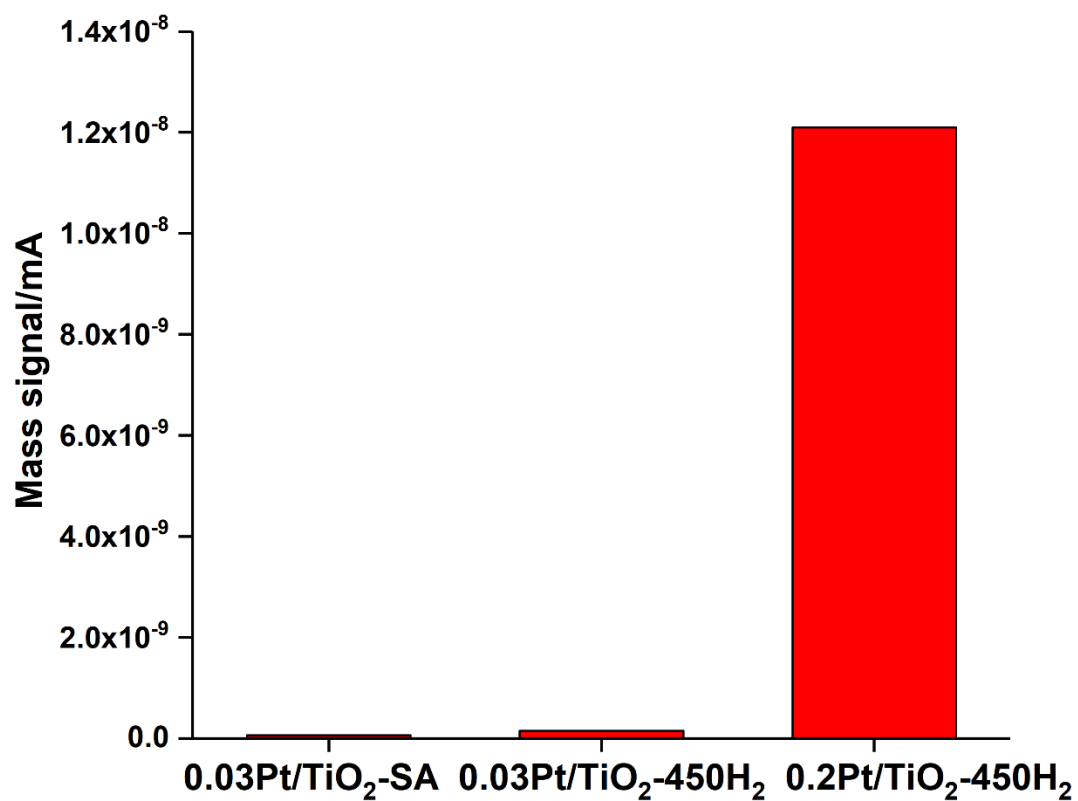


Figure S8. H₂-D₂ exchange activity on different types of Pt species supported on TiO₂ at room temperature. The formation rate of HD is expressed in this figure as the signal in mass spectrometer.

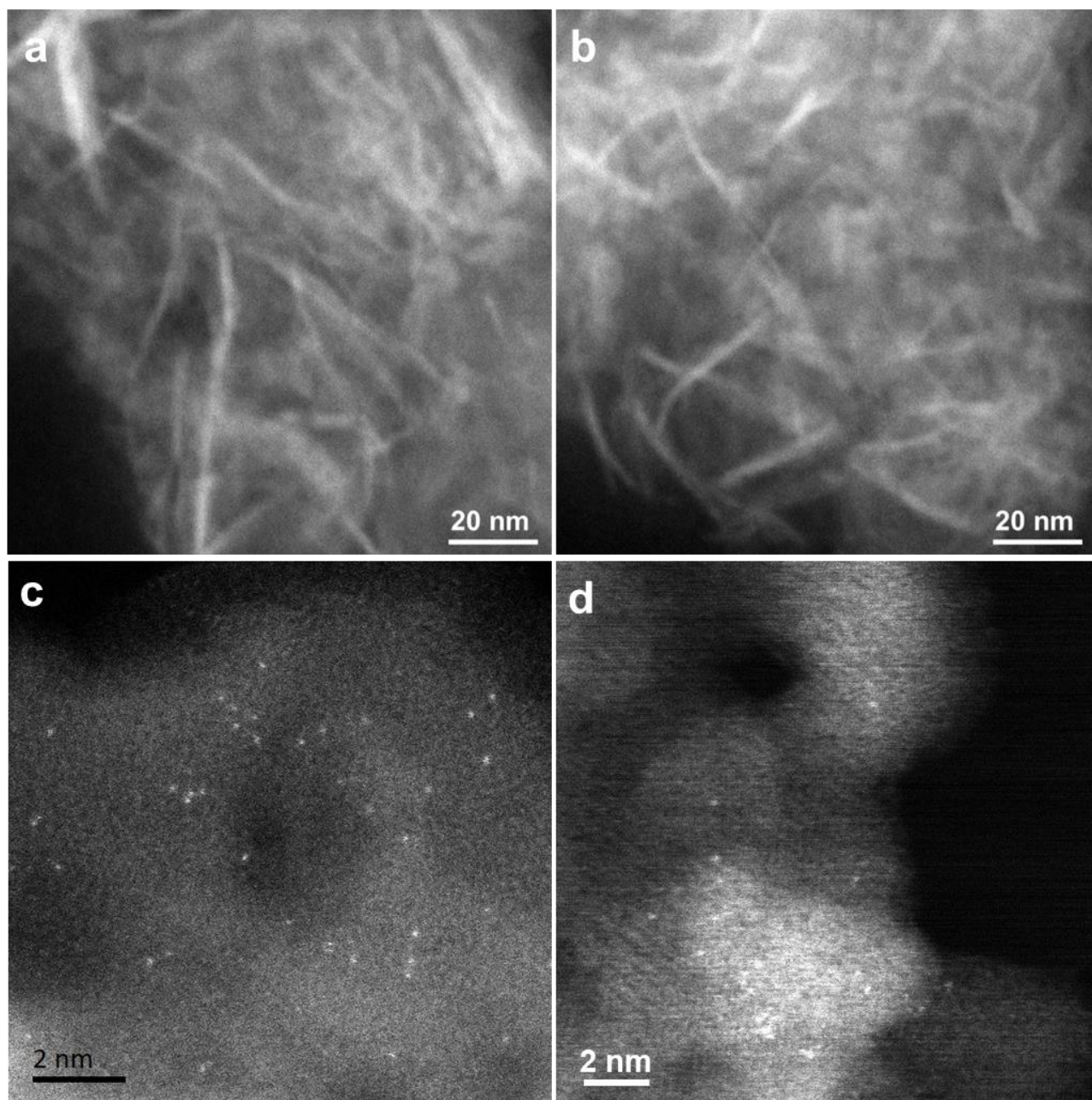


Figure S9. STEM image of as-prepared 0.2Pt/Al₂O₃-SA with atomically dispersed Pt species. No Pt nanoparticles can be observed in the fresh catalyst and Pt species exist as isolated Pt atoms on Al₂O₃ support.

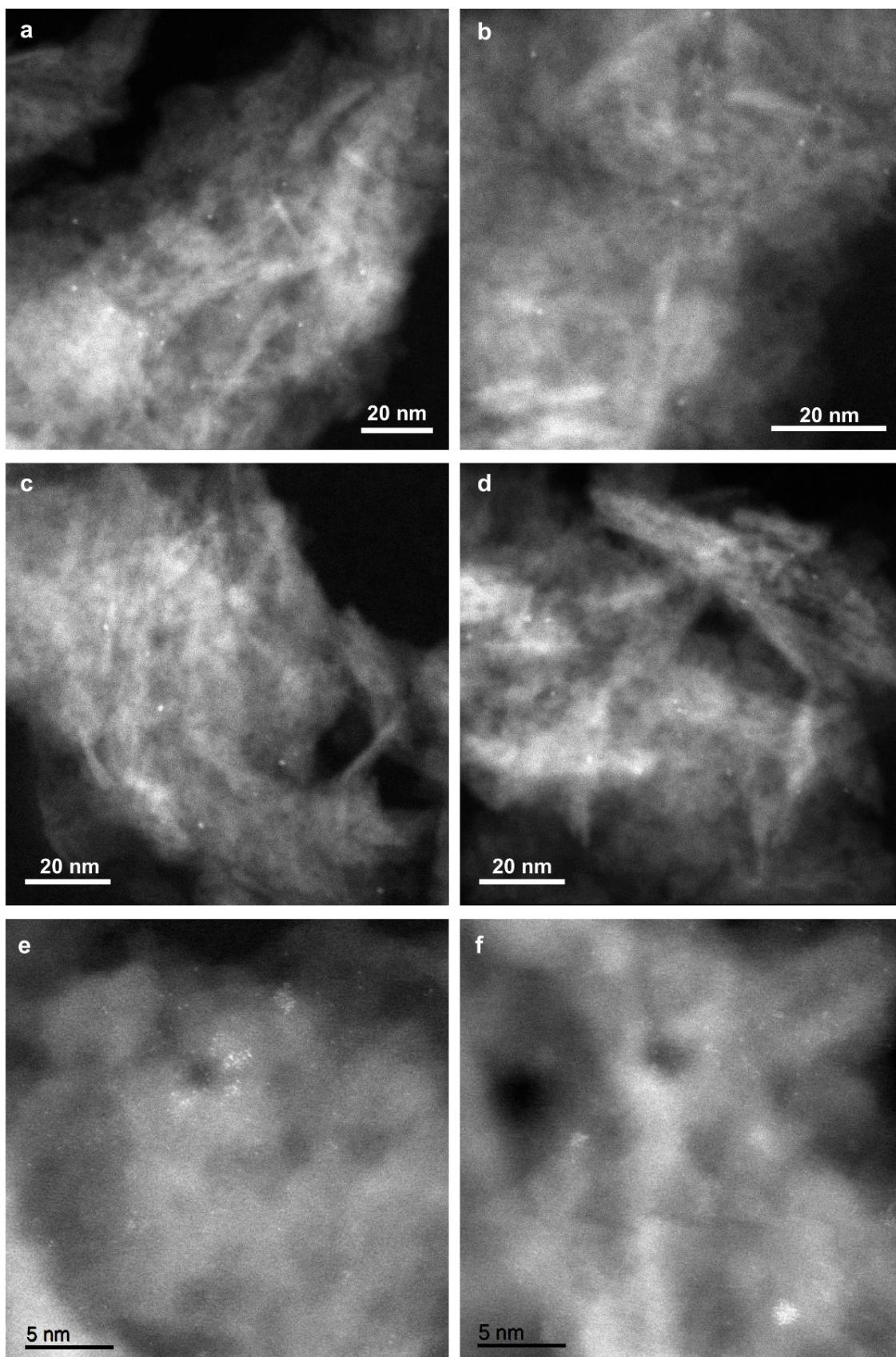


Figure S10. STEM images of 0.2Pt/Al₂O₃-200H₂ sample, showing the presence of both singly dispersed Pt atoms, Pt clusters and a few Pt nanoparticles.

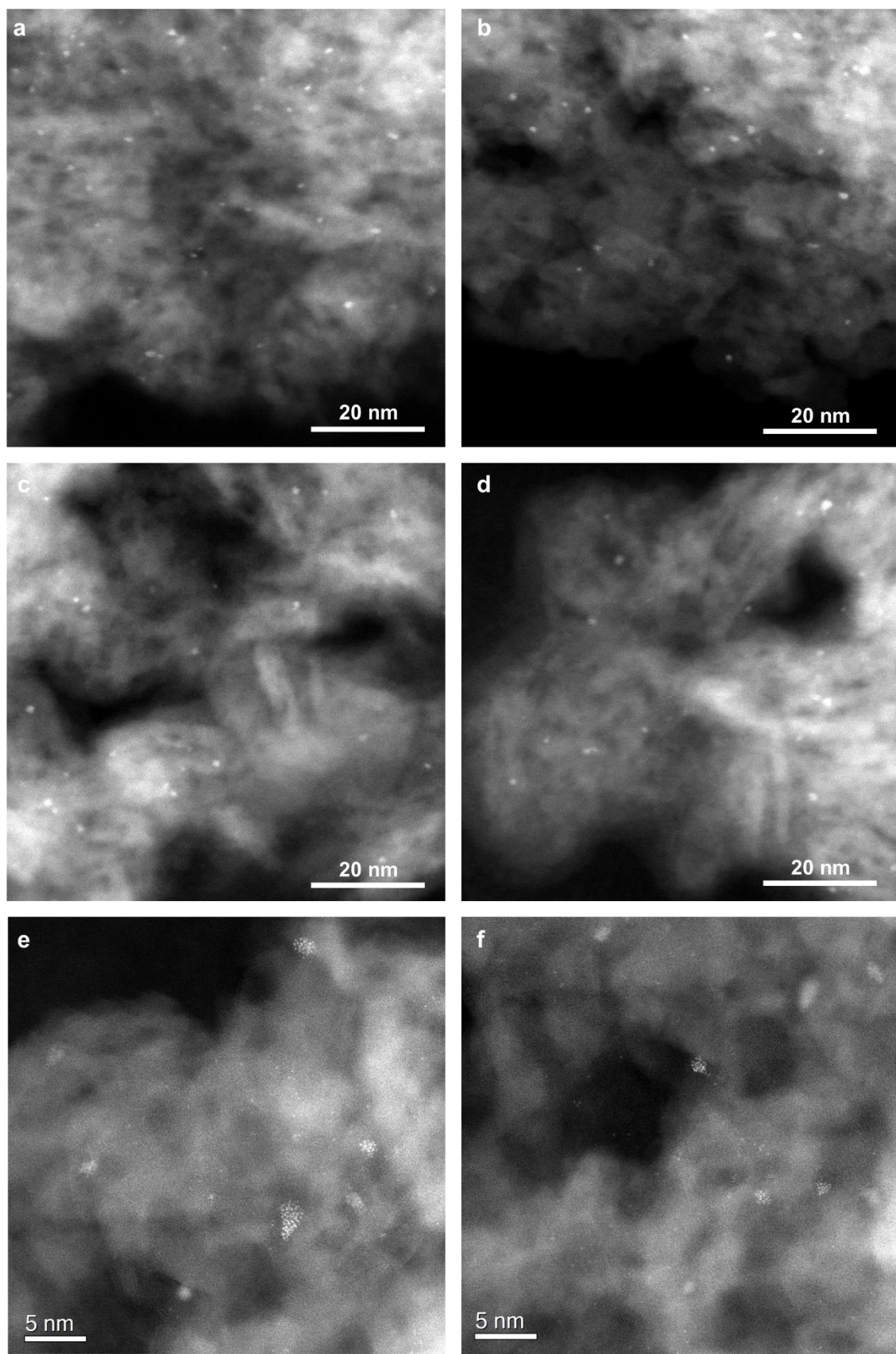


Figure S11. STEM images of 0.2Pt/Al₂O₃-300H₂ sample, showing the presence of a mixture of single Pt atoms, Pt clusters and nanoparticles.

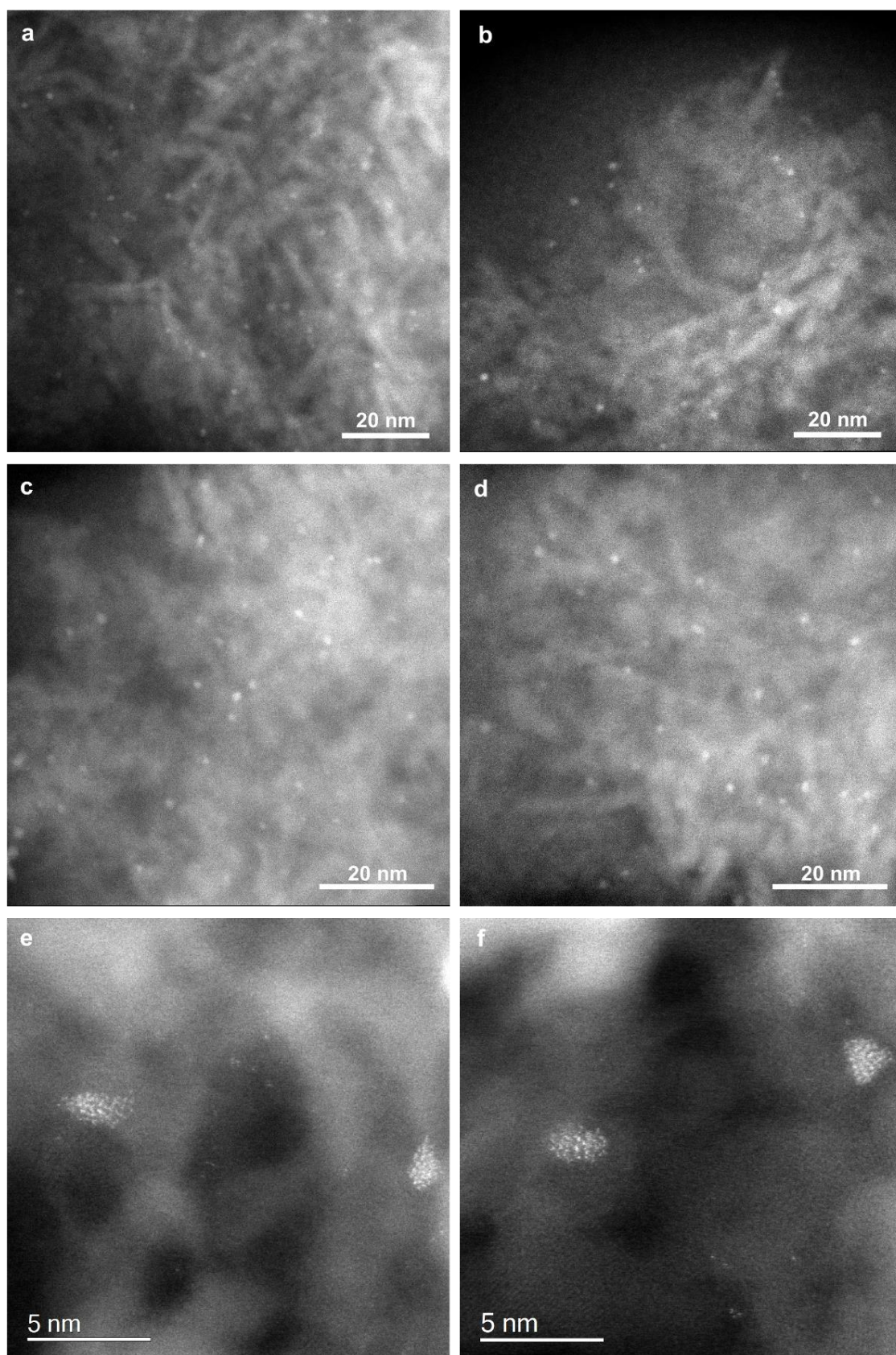


Figure S12. STEM images of 0.2Pt/Al₂O₃-450H₂ sample, showing the presence of a large fraction of Pt nanoparticles and a few single Pt atoms.

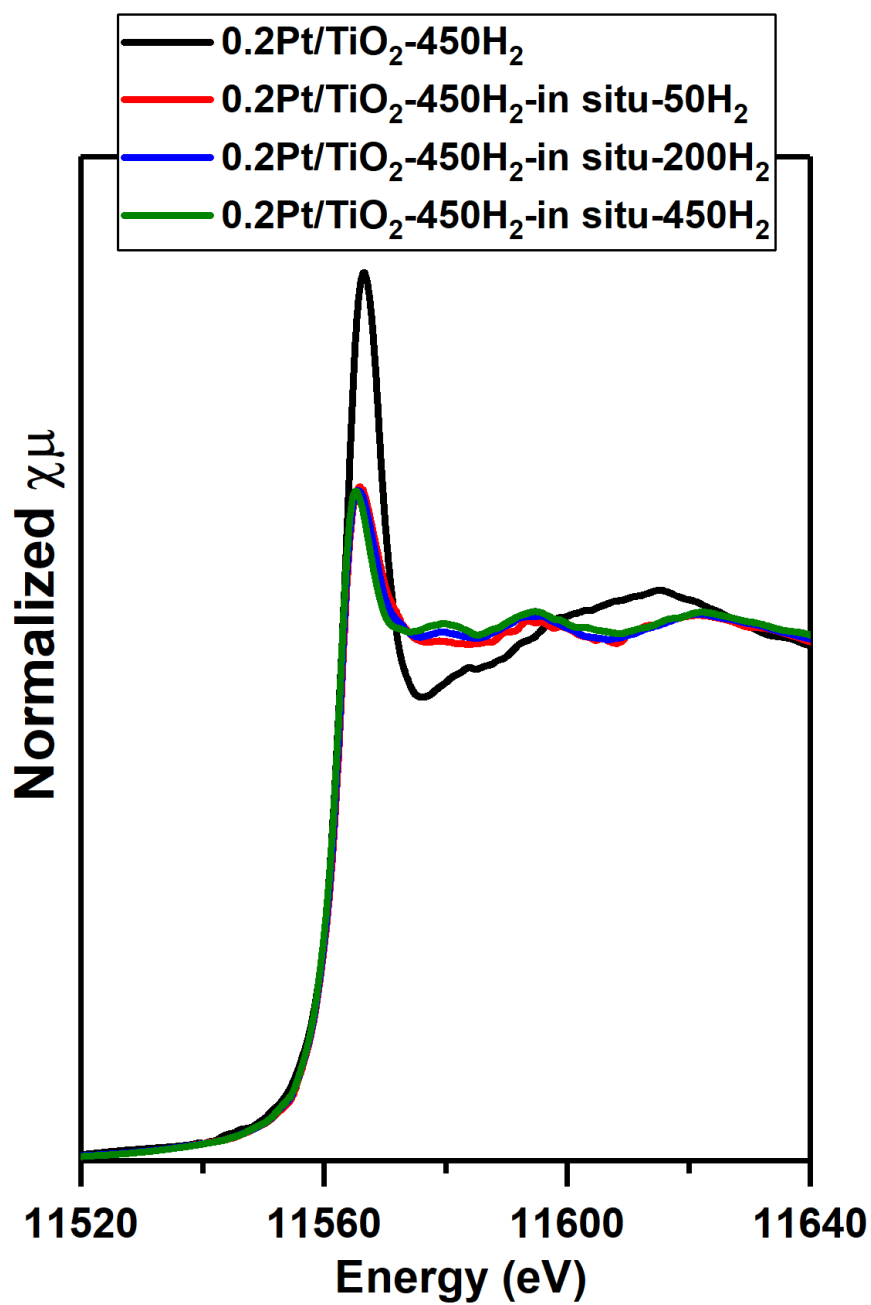


Figure S13. XANES spectra of the as-received 0.2Pt/TiO₂-450H₂ sample and the sample after pre-reduction treatment at different temperature. The spectra of Pt foil and PtO₂ reference are also included in this figure.

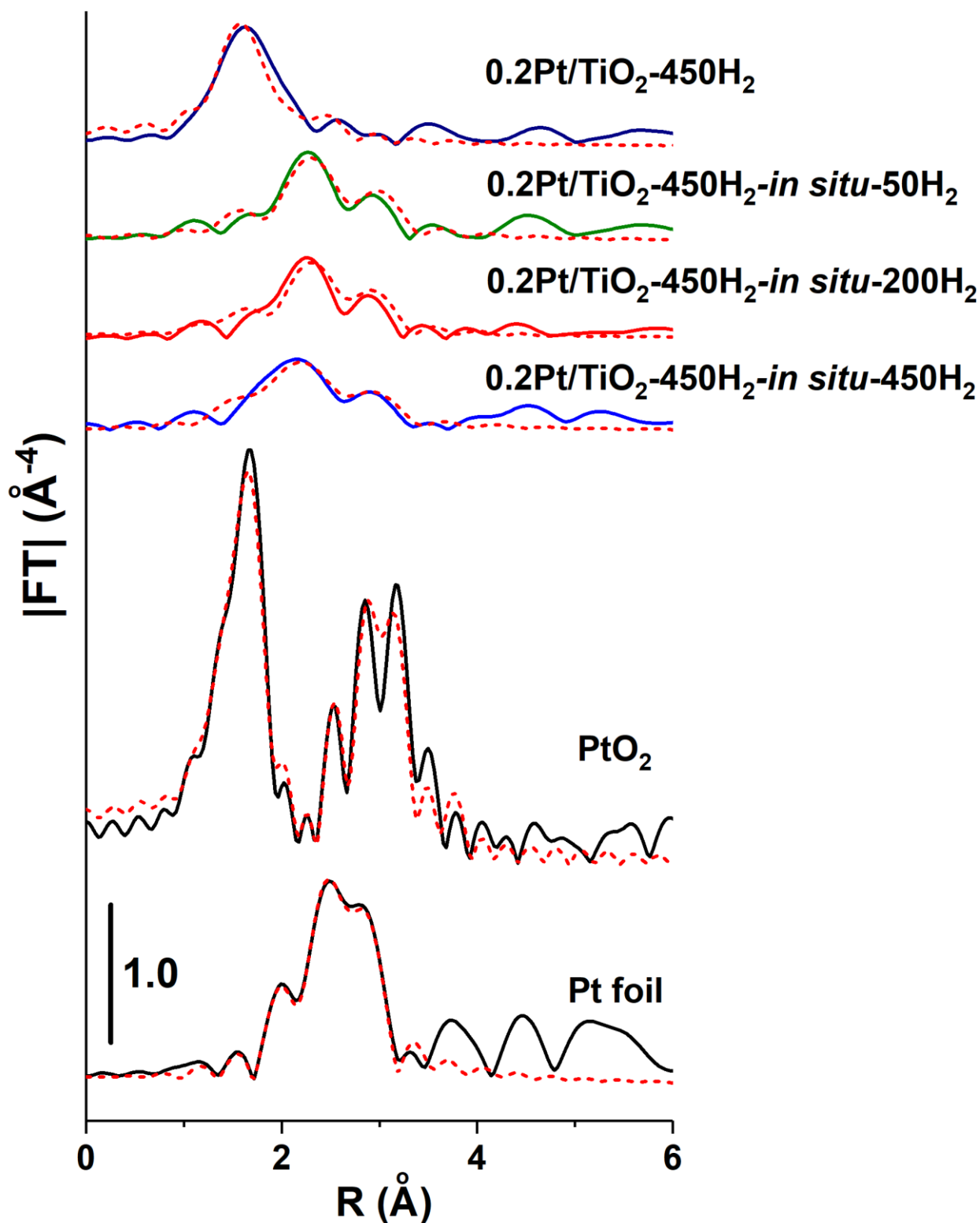


Figure S14. EXAFS spectra of the as-received 0.2Pt/TiO₂-450H₂ sample and the sample after pre-reduction treatment at different temperature. The spectra of Pt foil and PtO₂ reference are also included in this figure.

Table S1. Fit results of EXAFS spectra of the as-received 0.2Pt/TiO₂-450H₂ sample and the sample after pre-reduction treatment at different temperature.

Sample and treatment	N _{Pt-O}	R _{Pt-O}	N _{Pt-Ti}	R _{Pt-Ti}	N _{Pt-Pt}	R _{Pt-Pt}
Pt foil					12	2.77
PtO₂	6	1.99				
0.2Pt/TiO₂-450H₂	3.6 ± 0.5	1.99 ± 0.01	1.0 ± 0.5	2.61 ± 0.03		
0.2Pt/TiO₂-450H₂-in situ 50H₂	1 ± 1	2.0 ± 0.1			7 ± 1	2.77 ± 0.01
0.2Pt/TiO₂-450H₂-in situ 200H₂	0.8 ± 0.4	1.93 ± 0.05			5.6 ± 0.6	2.74 ± 0.01
0.2Pt/TiO₂-450H₂-in situ 450H₂	2 ± 1	2.04 ± 0.06			6 ± 1	2.72 ± 0.02

$\Delta E_0=9$, $R_{\text{factor}}=0.7$.

According to the fit results of the EXAFS spectra, the as-revised 0.2Pt/TiO₂-450H₂ sample showed a dominant contribution at ~ 2 Å, corresponding to Pt-O bonding. Such feature in the EXAFS spectra of the as-received sample should be caused by the re-oxidation of small Pt nanoparticles in air. After reduction by H₂ at 50 °C, the as-received 0.2Pt/TiO₂-450H₂ sample will be almost completed reduced to metallic Pt, with a low Pt-O coordination number associated with the Pt-O-Ti interfacial structure. Interestingly, when the pre-reduction temperature was increased to 450 °C, a higher Pt-O contribution is observed. Considering we have observed the partial decoration of Pt particles by TiO₂ overlayers in the 0.2Pt/TiO₂-450H₂ sample, the Pt-O contribution should be related to the strong metal-support interaction between Pt and TiO₂ overlayers.

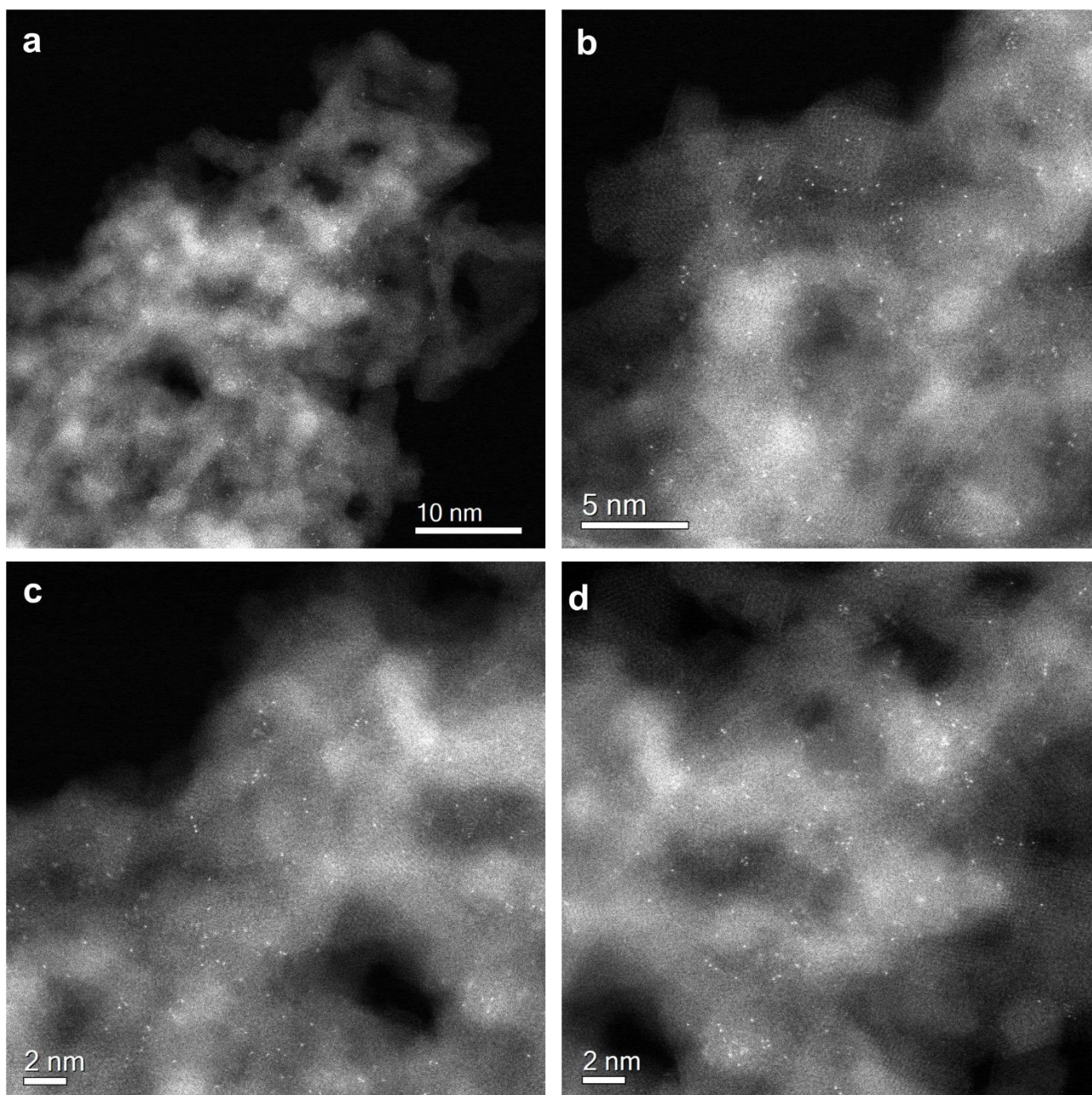


Figure S15. High-resolution STEM image of Pt/Al₂O₃-SA sample after the hydrogenation of 3-nitrostyrene reaction. These images confirm the stability of single Pt atoms under mild reaction conditions.

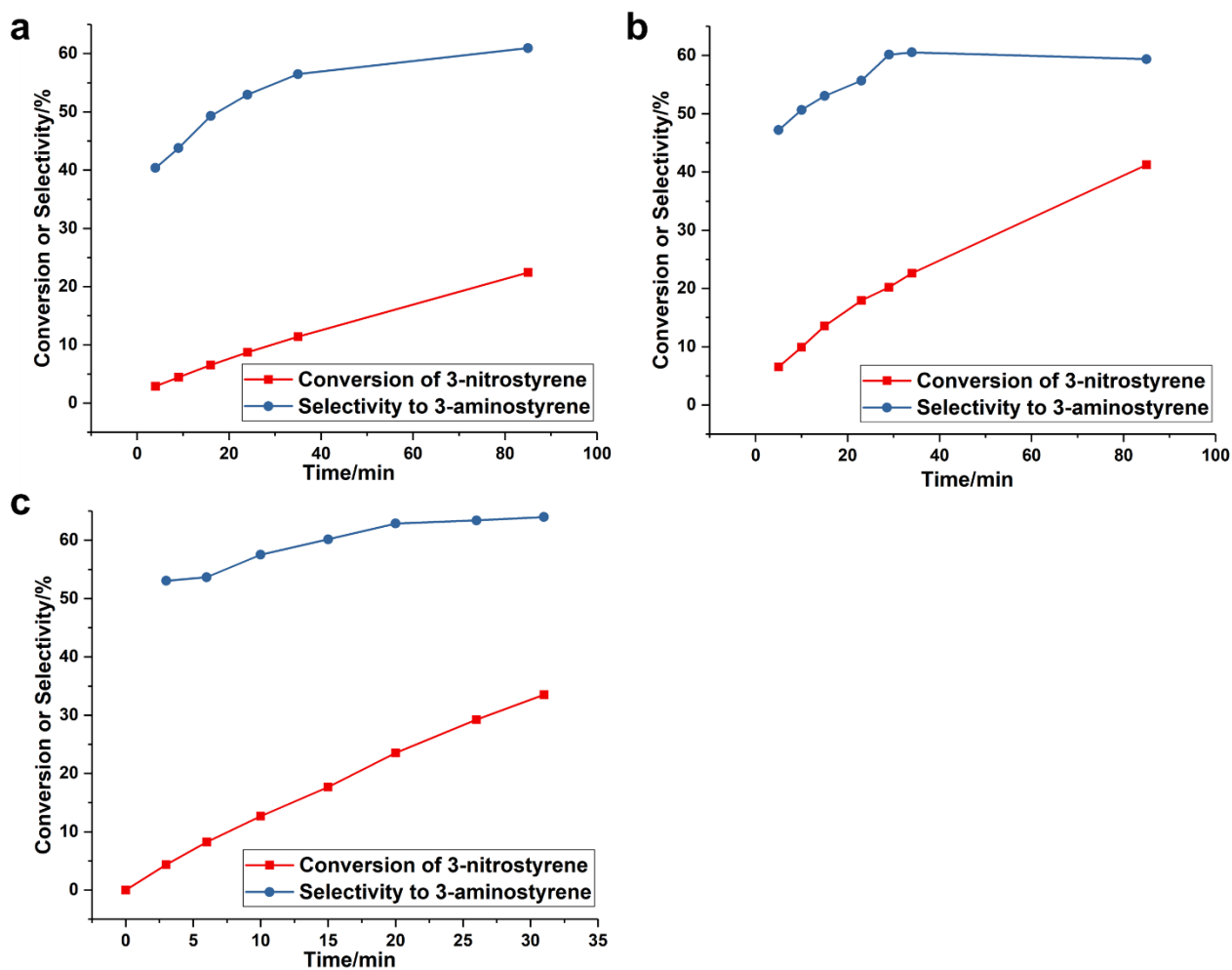


Figure S16. Hydrogenation of 3-nitrostyrene with various 0.2Pt/Al₂O₃ catalysts. Reaction conditions: 0.5 mmol 3-nitrostyrene, 2 mL toluene as solvent, 20 mg of solid catalyst, 50 °C and 3 bar of H₂. (a) 0.2Pt/Al₂O₃-200H₂, (b) 0.2Pt/Al₂O₃-300H₂ and (c) 0.2Pt/Al₂O₃-4500H₂.

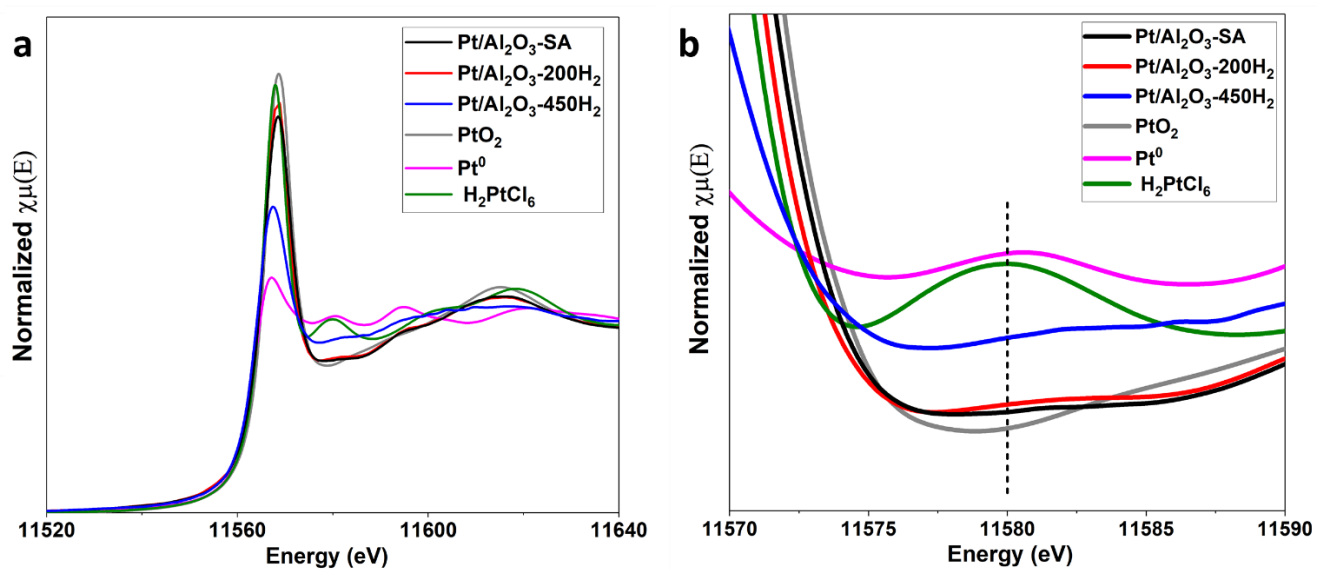


Figure S17. (a) XANES spectra of Pt/Al₂O₃ samples and the references (Pt⁰, PtO₂ and H₂PtCl₆). (b) Enlarged XANES spectra at ~11580 eV, showing the absence of Pt-Cl bonding in Pt/Al₂O₃ samples.

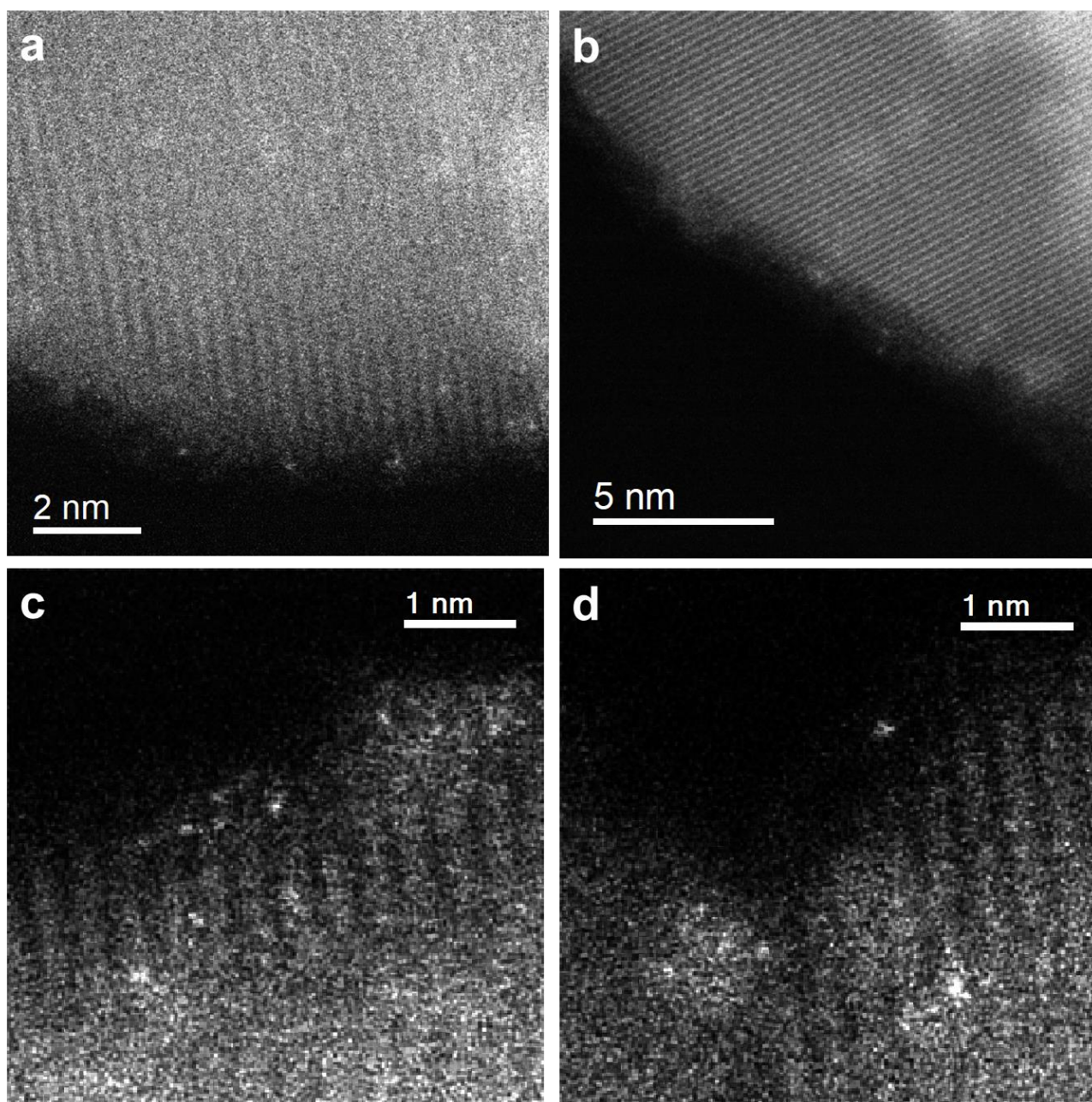


Figure S18. STEM images of 0.04%Pt/TiO₂-acac-SA sample prepared by impregnation using Pt(acac)₂ as precursor. Singly dispersed Pt atoms can be observed in this sample.

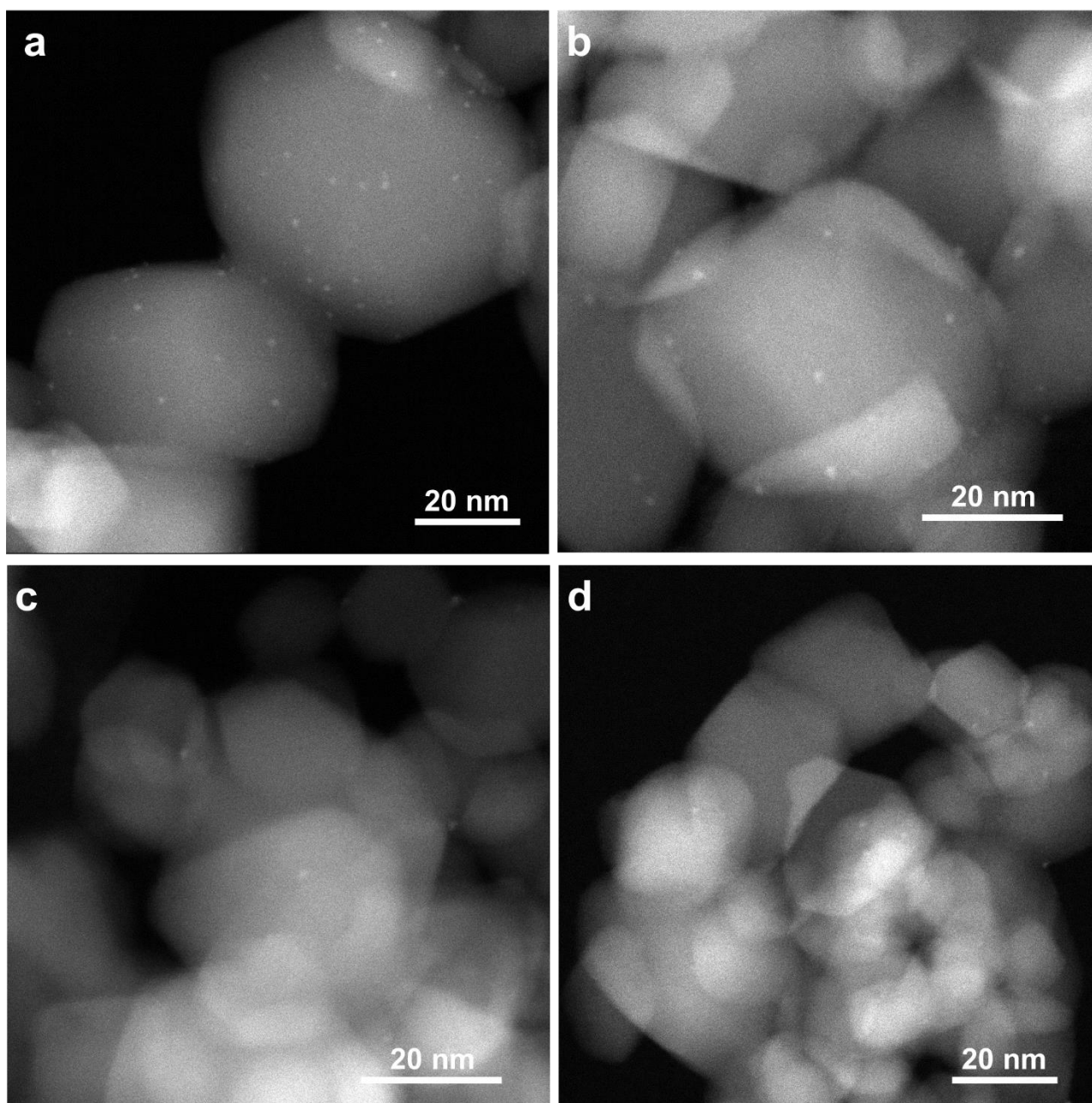


Figure S19. STEM images of 0.04%Pt/TiO₂-acac-450H₂ sample prepared by impregnation using Pt(acac)₂ as precursor.

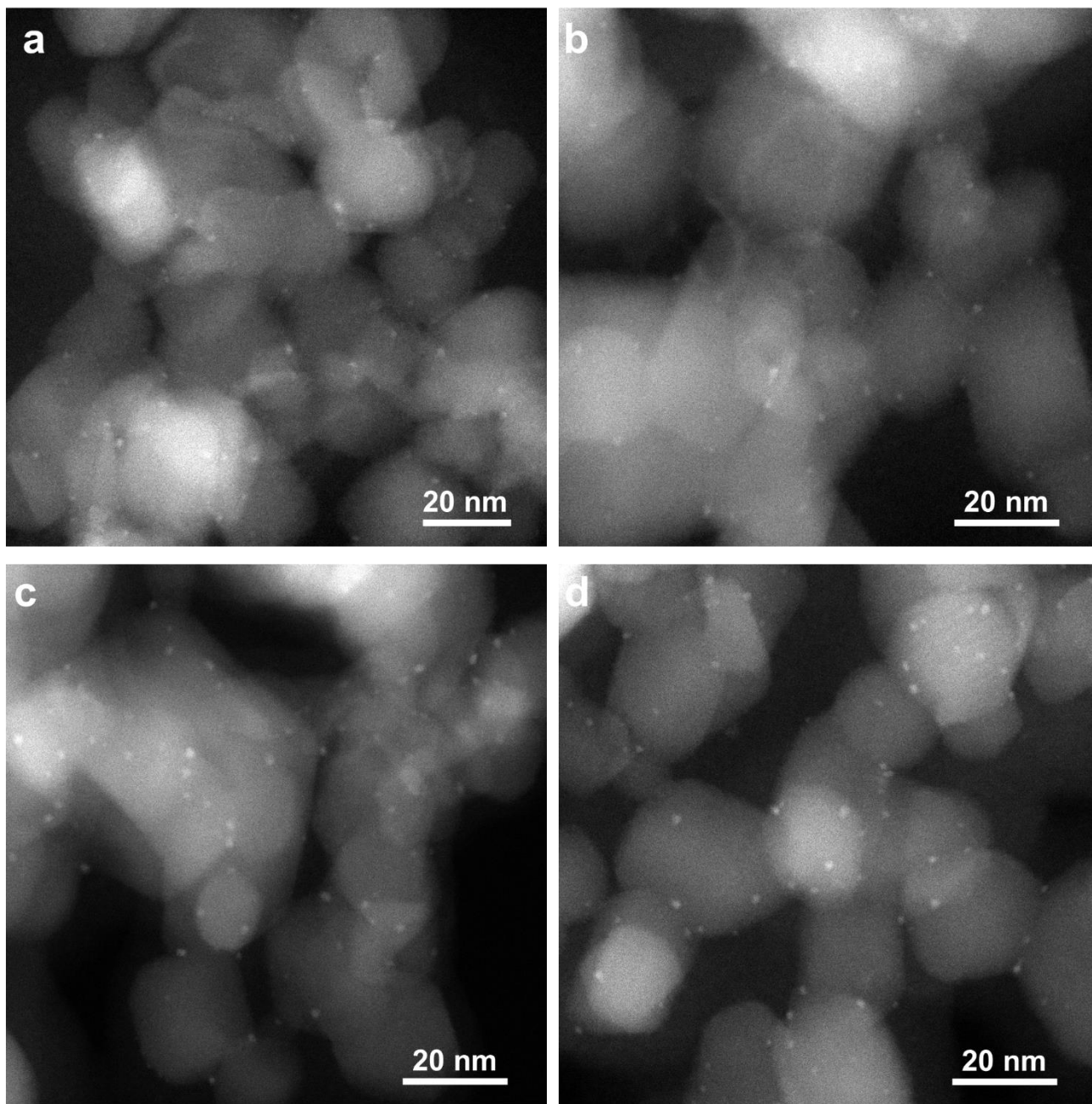


Figure S20. STEM images of 0.25%Pt/TiO₂-acac-450H₂ sample prepared by impregnation using Pt(acac)₂ as precursor.

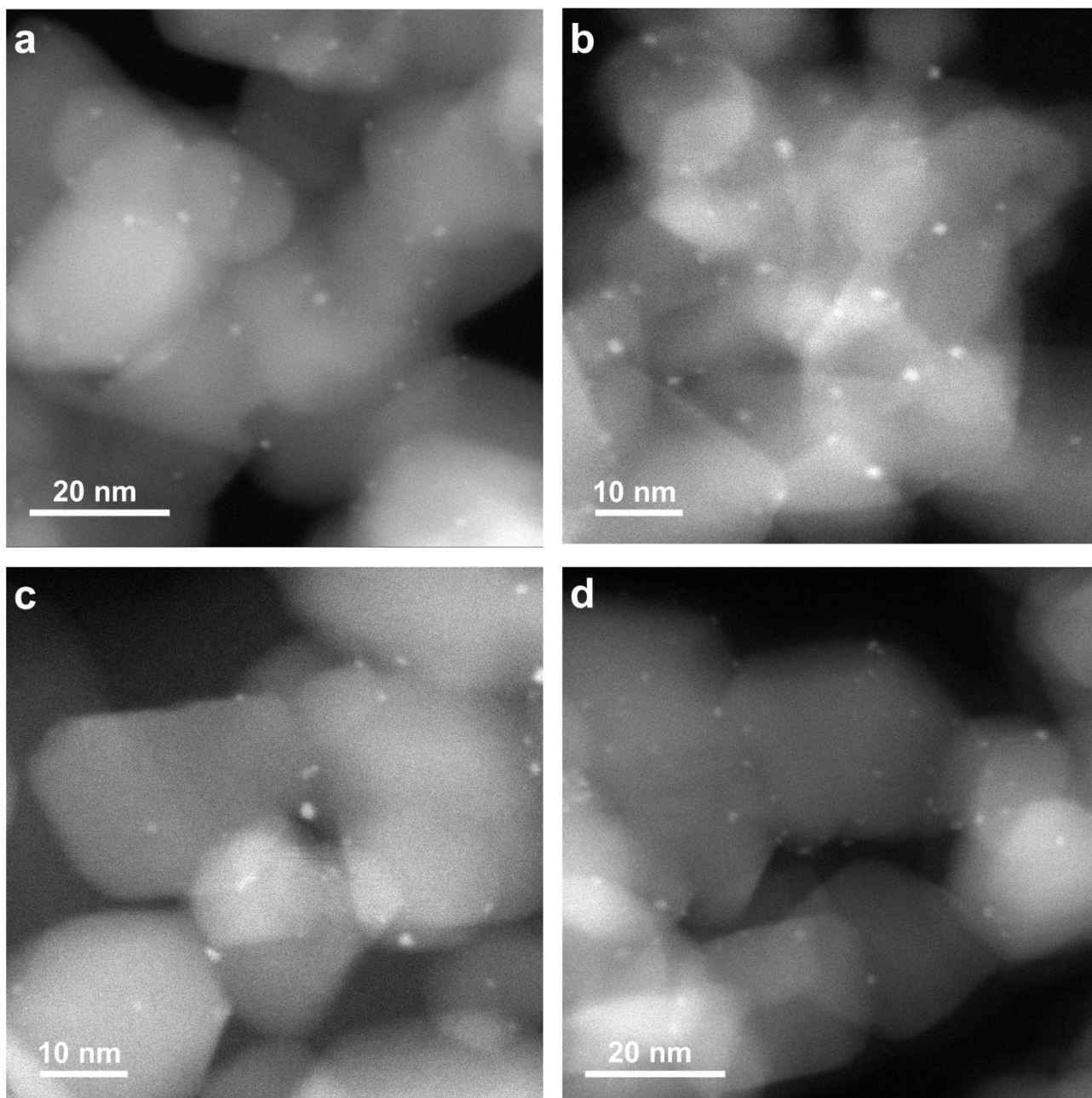


Figure S21. STEM images of 0.5%Pt/TiO₂-acac-450H₂ sample prepared by impregnation using Pt(acac)₂ as precursor.

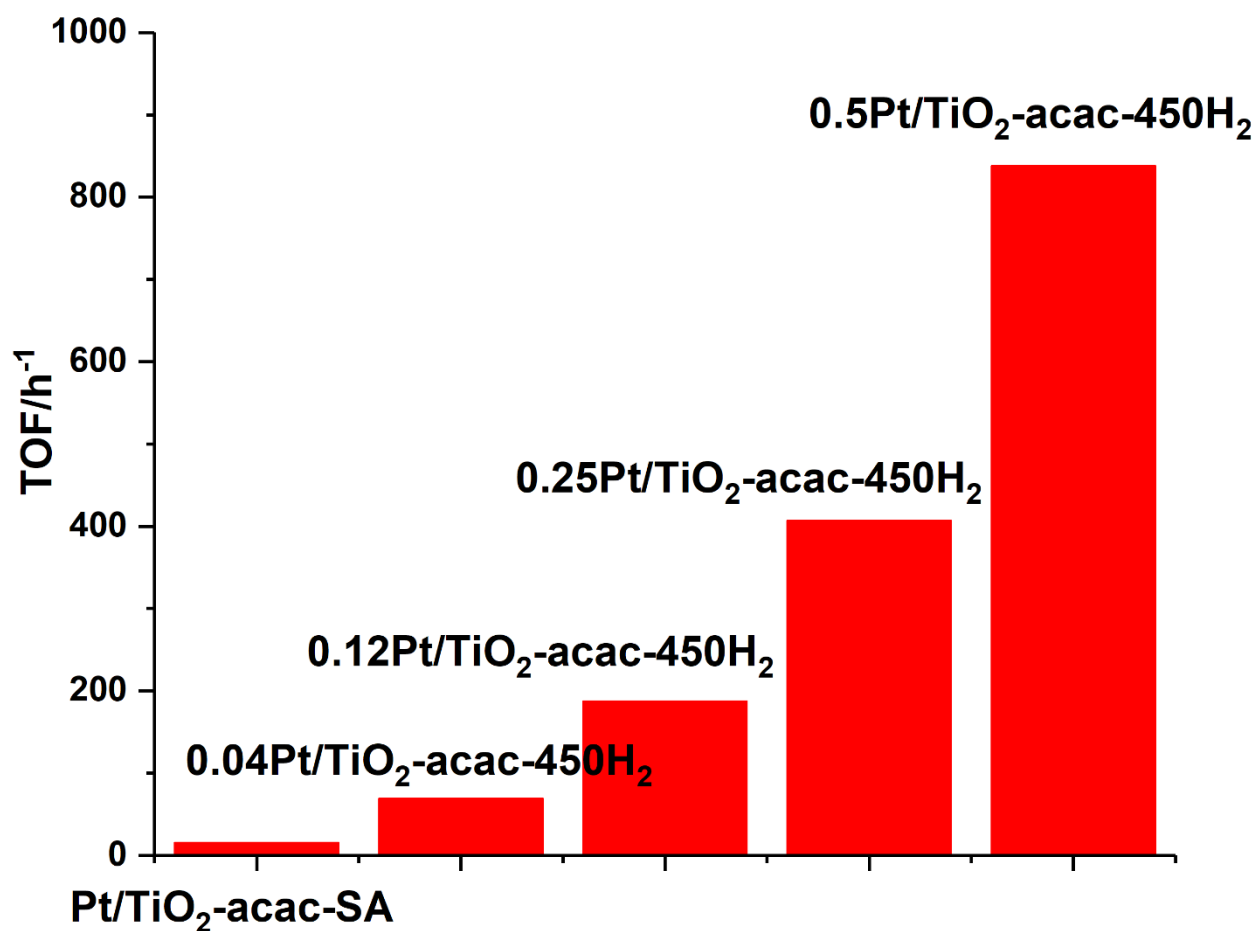


Figure S22. Catalytic performance of Pt/TiO₂ samples prepared by impregnation and using Pt(acac)₂ as the Pt precursor for hydrogenation of 3-nitrostyrene. Reaction conditions: 40 °C, 3 bar of H₂, 10 mg of solid catalyst, 0.5 mmol of 3-nitrostyrene and 2 mL toluene as solvent.

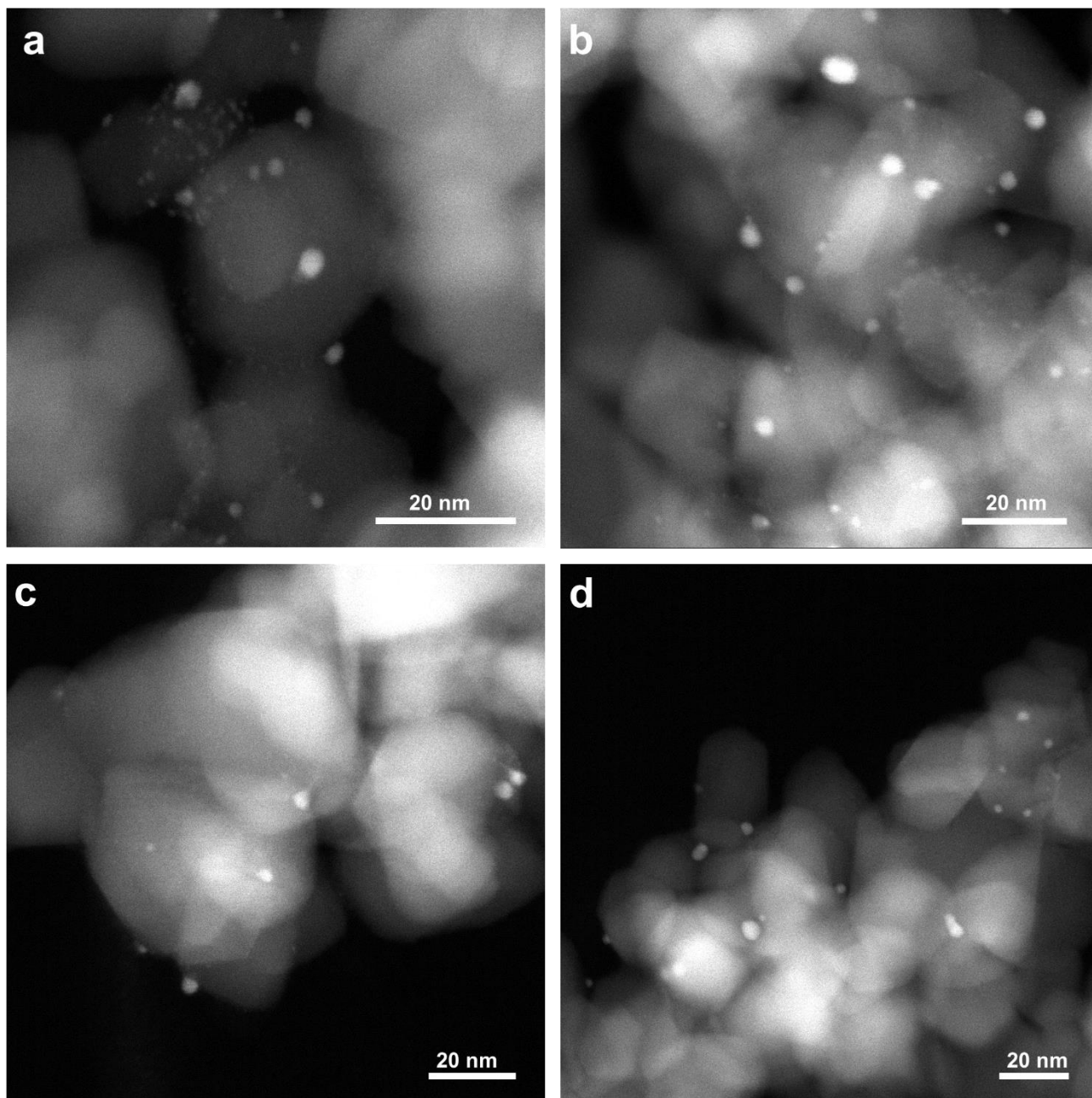


Figure S23. STEM images of PtNP/TiO₂-air sample prepared by deposition of Pt nanoparticles on TiO₂ support. The PVP polymer used in the synthesis of Pt colloid nanoparticles was removed by calcination in air. Pt nanoparticles of 1-5 nm dispersed on TiO₂ can be observed in this sample.

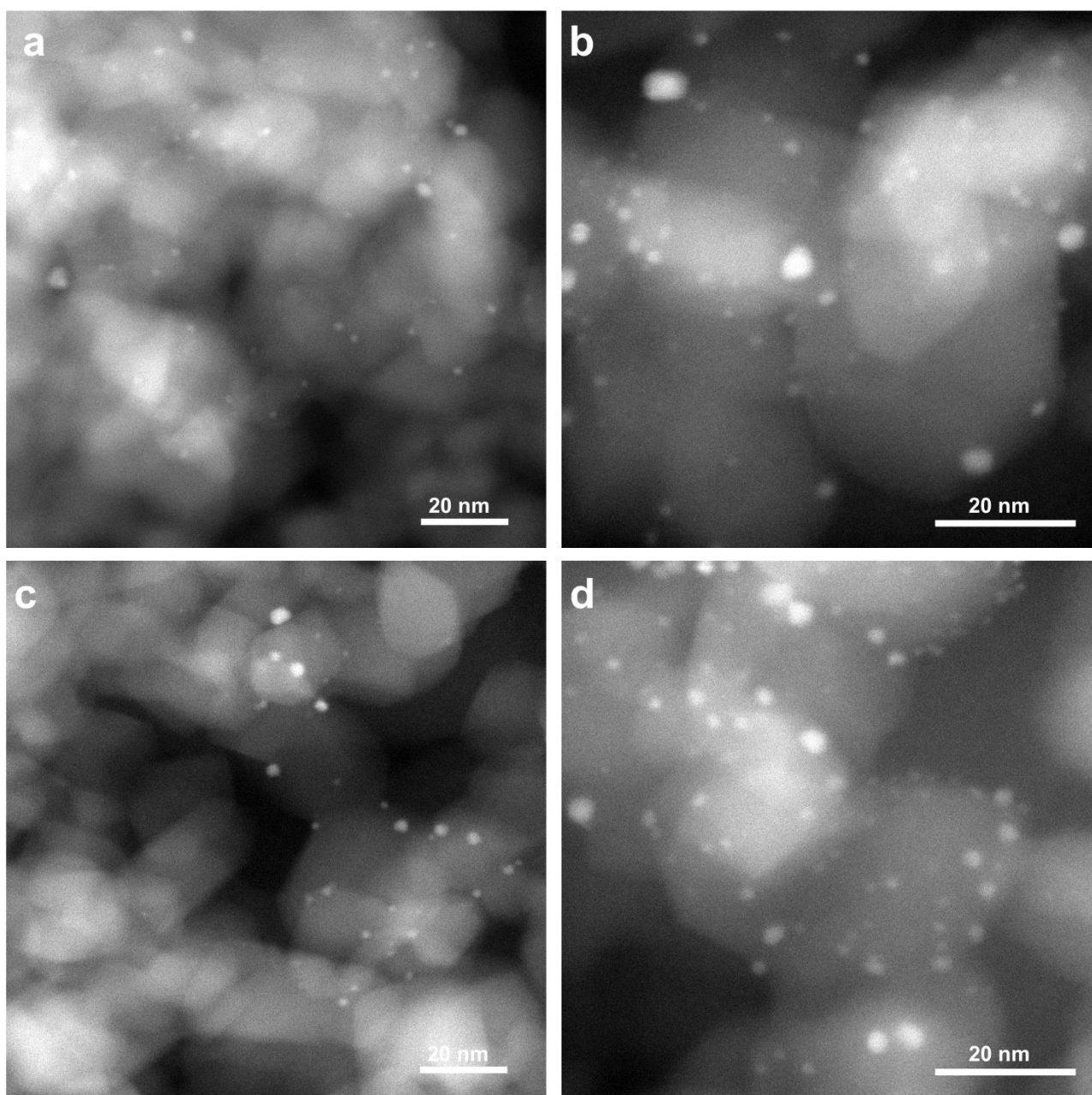


Figure S24. STEM images of PtNP/TiO₂-450H₂ sample obtained by reducing the PtNP/TiO₂-air sample by H₂ at 450 °C. Pt nanoparticles of 1-5 nm dispersed on TiO₂ can be observed in this sample.

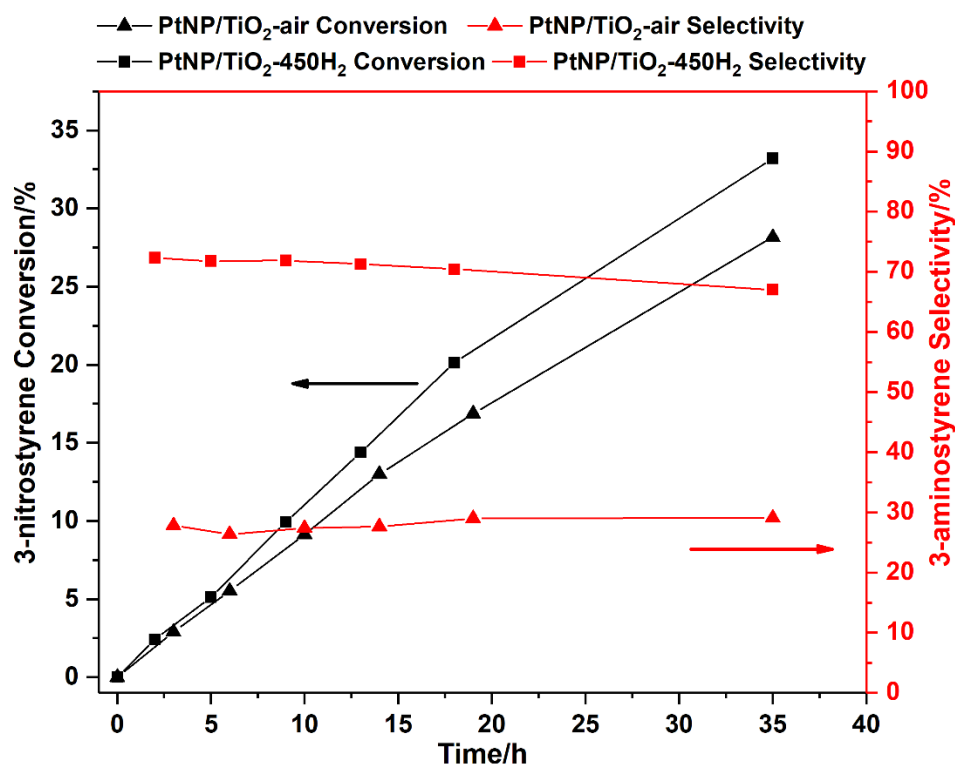


Figure S25. Catalytic performance of PtNP/TiO₂-air and PtNP/TiO₂-450H₂ for hydrogenation of 3-nitrostyrene. Reaction conditions: 40 °C, 3 bar of H₂, 10 mg of solid catalyst, 0.5 mmol of 3-nitrostyrene and 2 mL toluene as solvent.

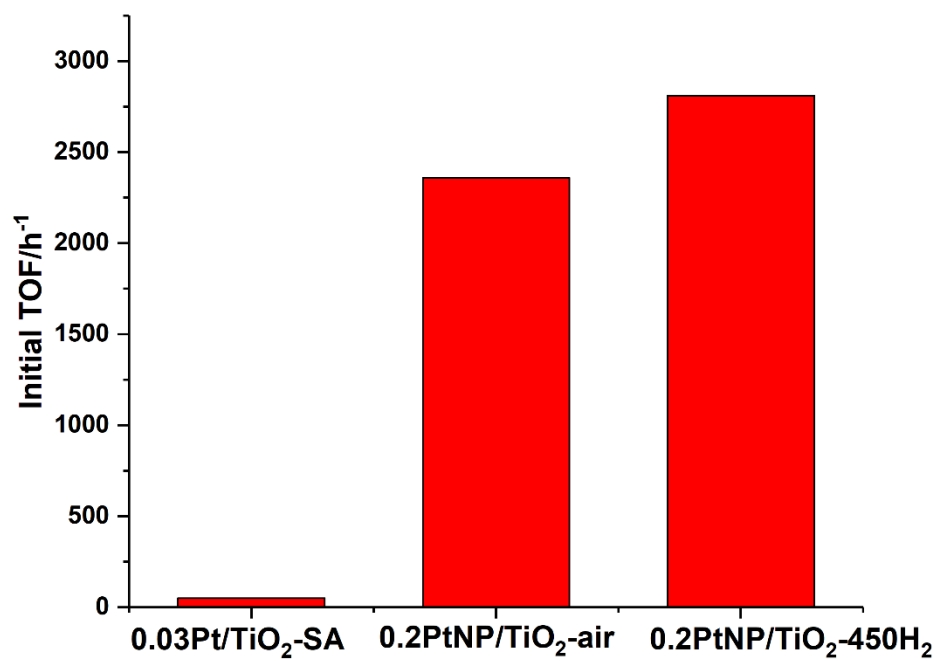


Figure S26. Initial TOF of PtNP/TiO₂-air and PtNP/TiO₂-450H₂ for hydrogenation of 3-nitrostyrene.

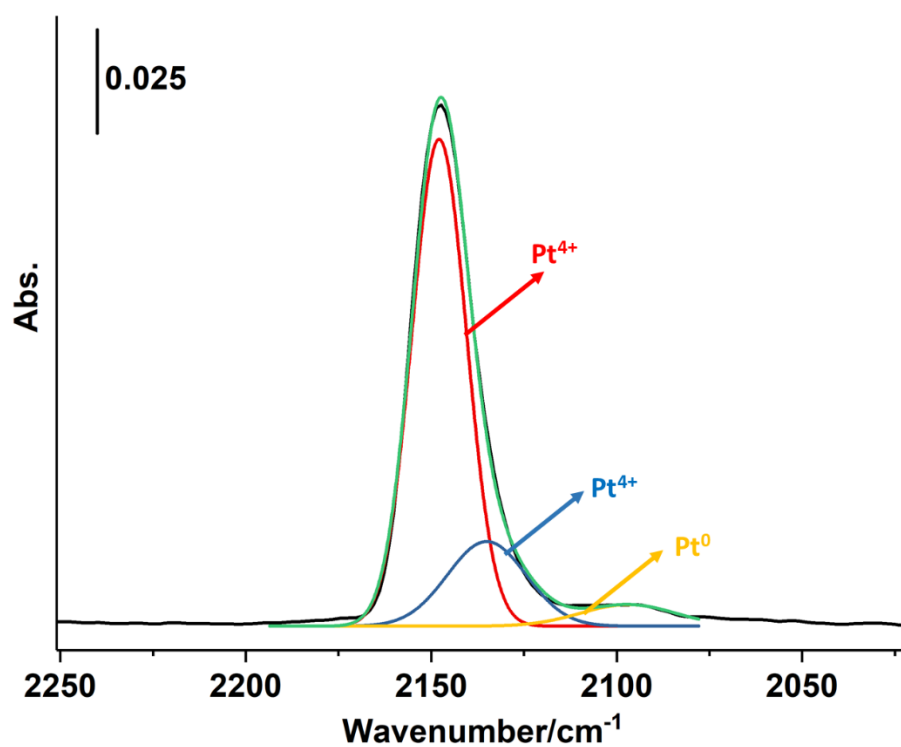


Figure 27. CO-IR spectra of the Pt/Al₂O₃-SA sample obtained at low temperature (-170 °C). The majority of the Pt species exist as cationic Pt atoms in the fresh Pt/Al₂O₃-SA sample.

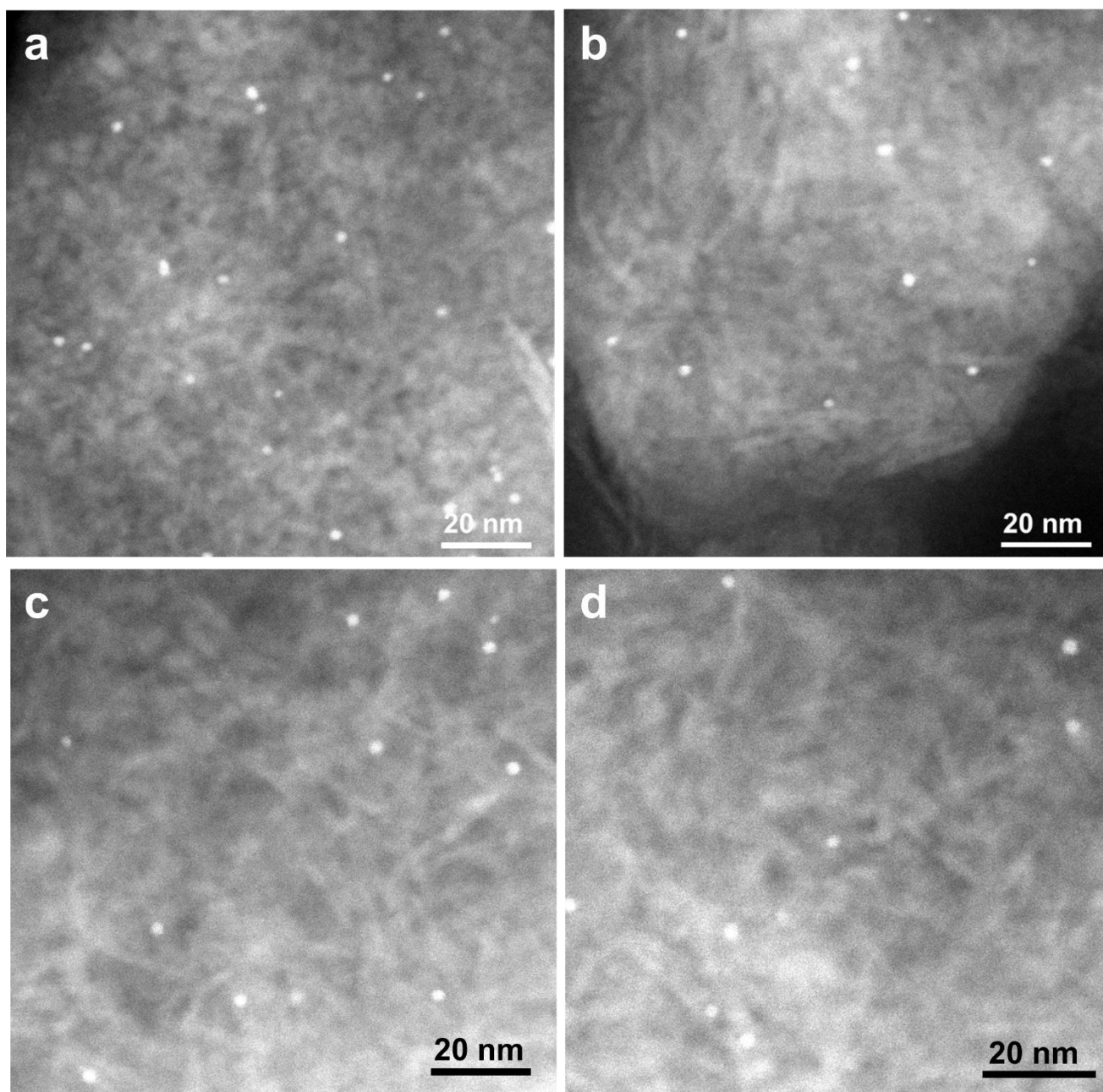


Figure S28. STEM image of 0.2Pt/Al₂O₃-SA catalyst after CO+O₂ reaction at 325 °C. Pt nanoparticles can be observed in the fresh catalyst.

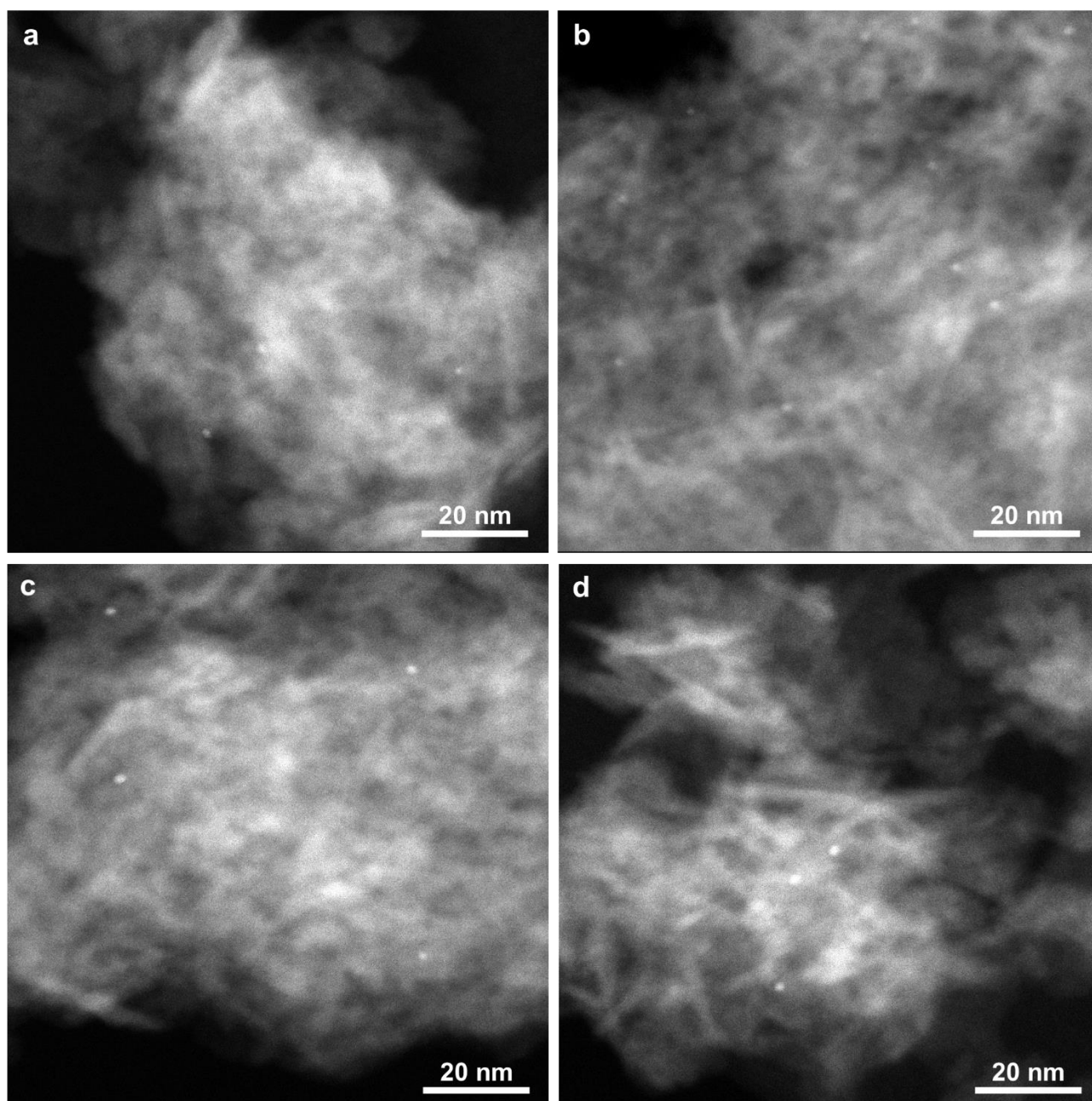


Figure S29. STEM images of 0.2Pt/Al₂O₃-SA sample after CO oxidation at 150 °C. A few small Pt nanoparticles can be observed in the used catalyst.

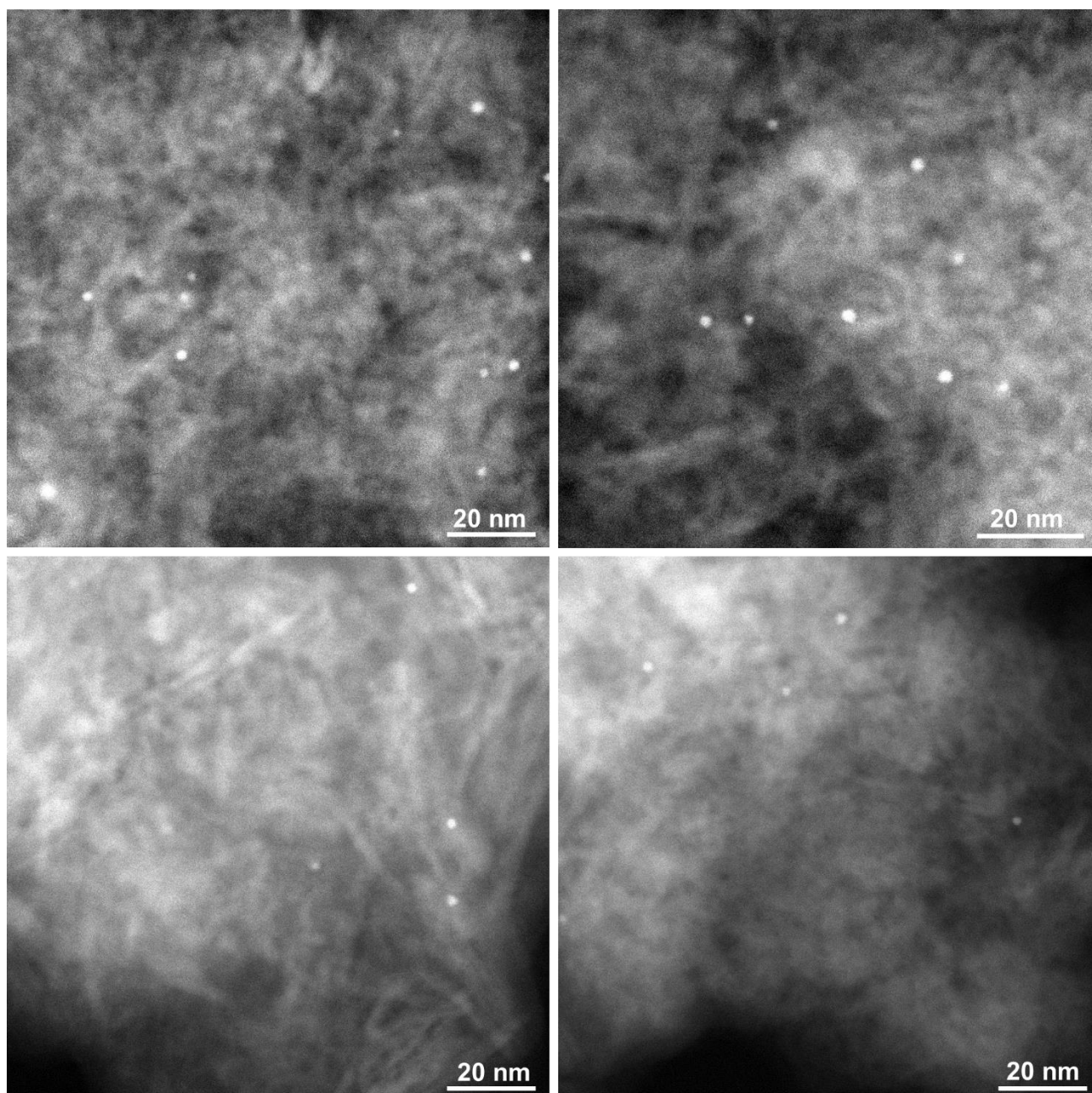


Figure S30. STEM images of 0.2Pt/Al₂O₃-SA sample after CO oxidation at 225 °C. Pt nanoparticles can be observed in the used catalyst, due to the agglomeration of highly dispersed Pt atoms.

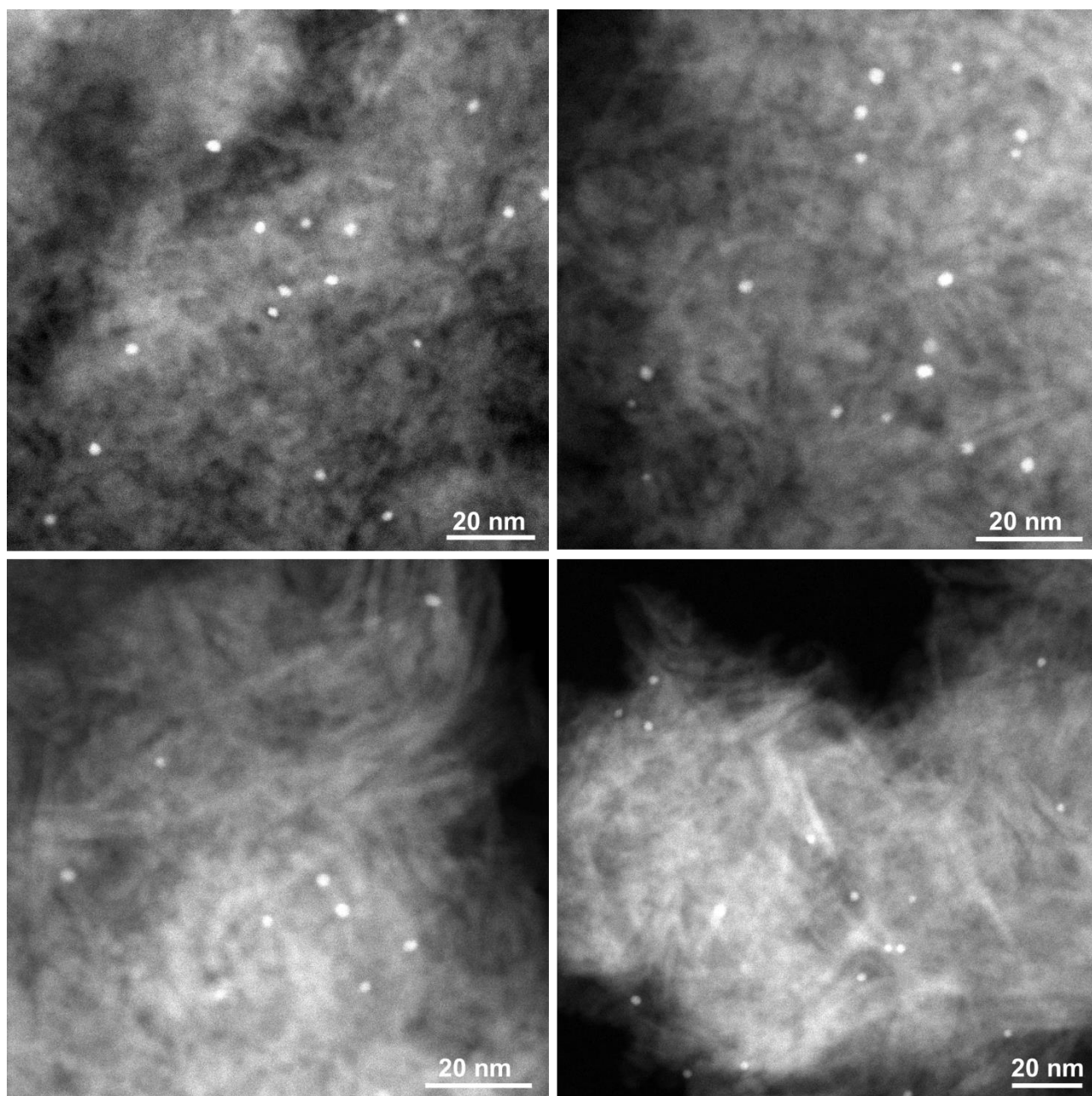


Figure S31. STEM images of 0.2Pt/Al₂O₃-SA sample after CO oxidation at 275 °C. Pt nanoparticles can be observed in the used catalyst, due to the agglomeration of highly dispersed Pt atoms.

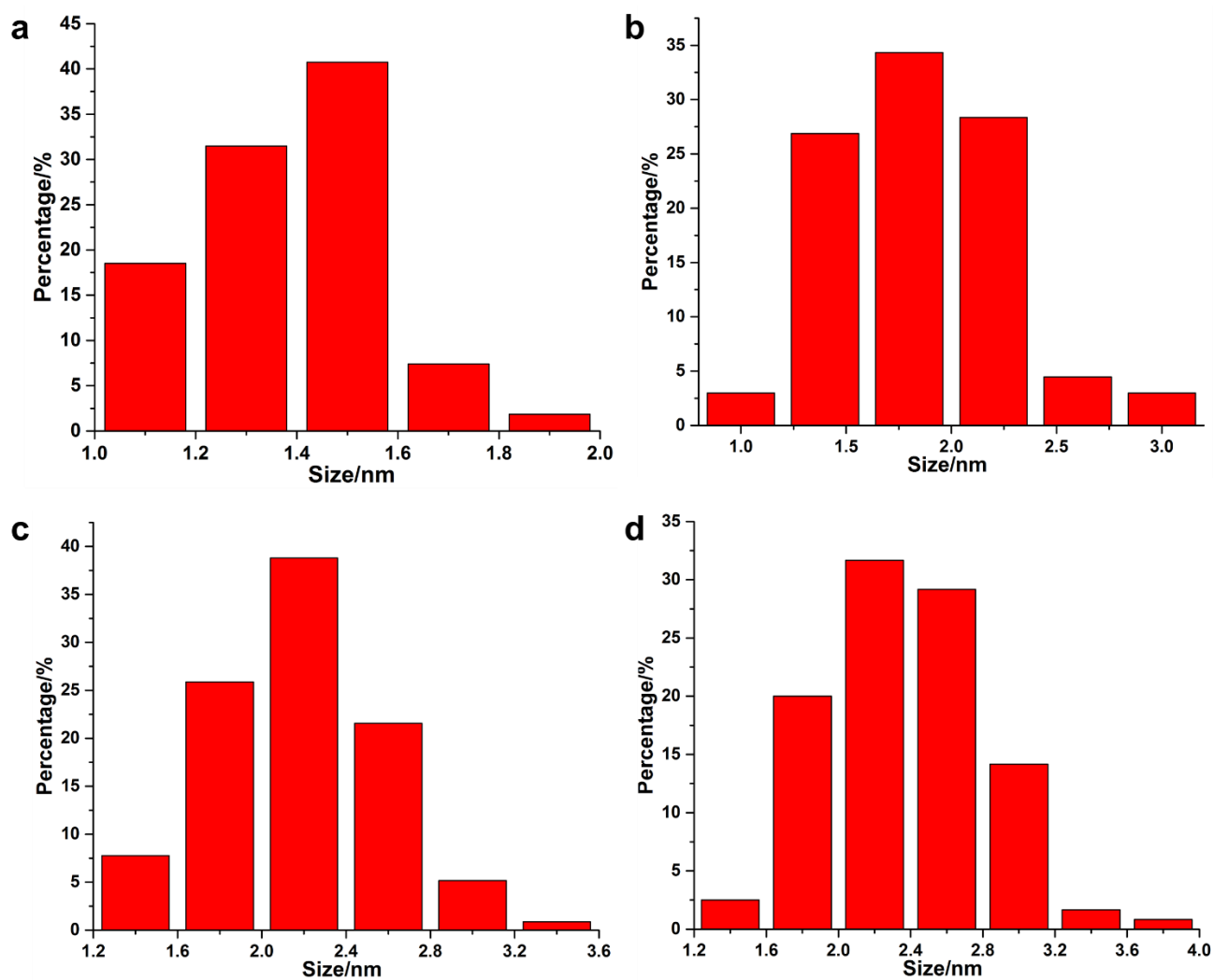


Figure S32. Size distributions of Pt nanoparticles observed in Pt/Al₂O₃-SA sample after CO oxidation reaction at different temperature. (a) 150 °C, (b) 225 °C, (c) 275 °C and (d) 325 °C.

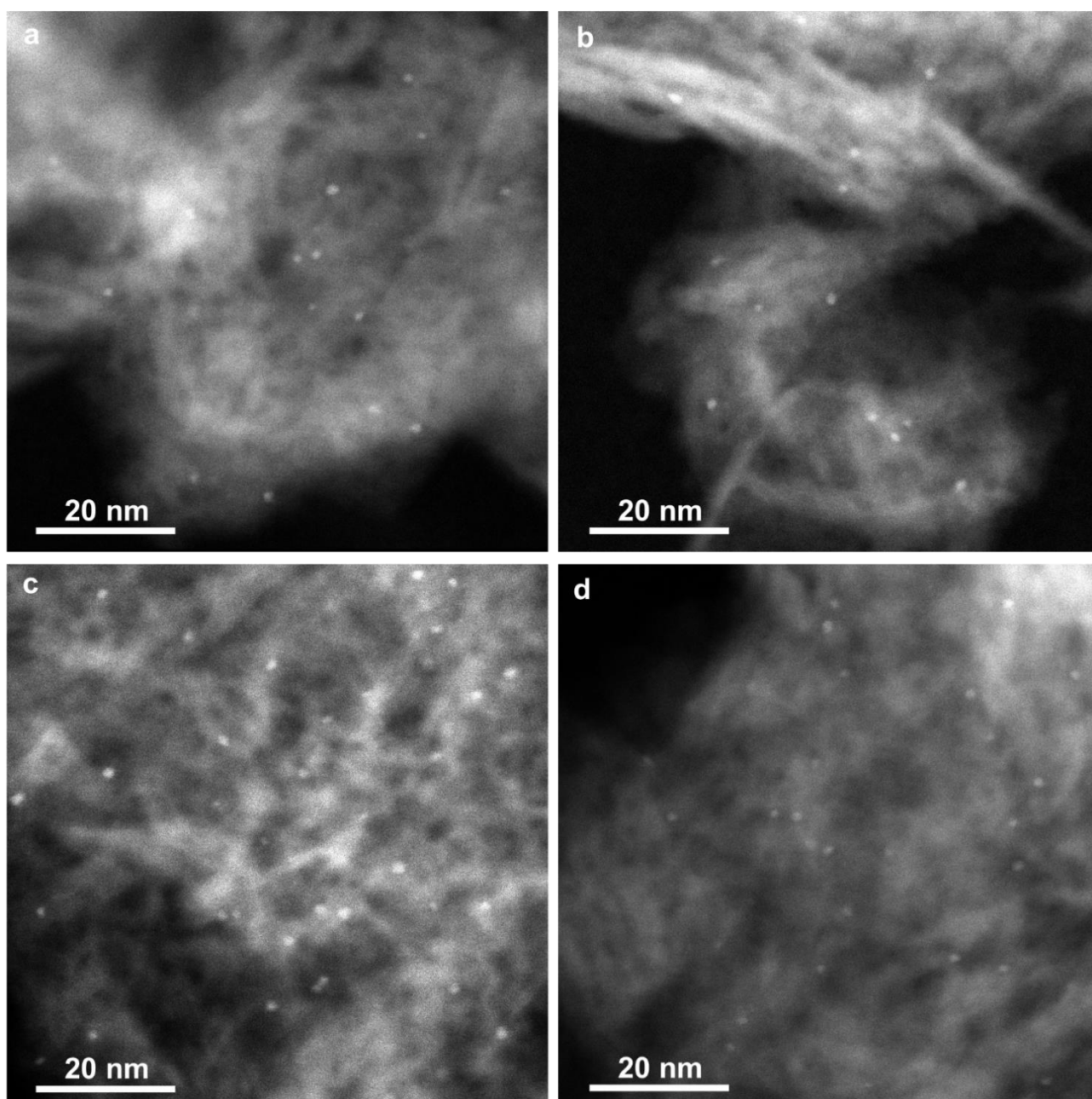


Figure S33. STEM images of 0.2Pt/Al₂O₃-200H₂ sample after CO oxidation reaction at 325 °C. As can be seen, the size of Pt increases slightly compared to the pristine 0.2Pt/Al₂O₃-200H₂ sample.

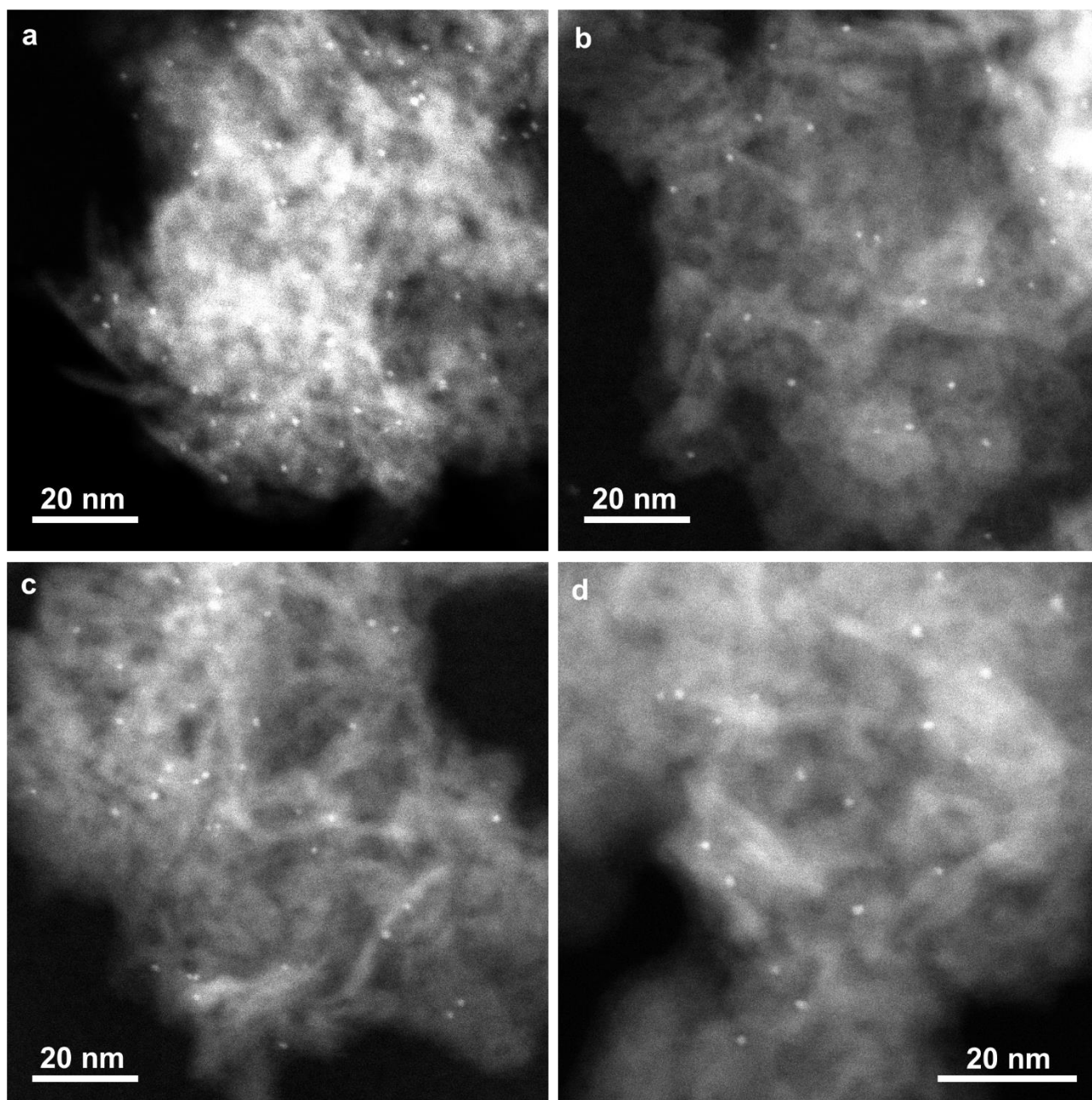


Figure S34. STEM images of 0.2Pt/Al₂O₃-300H₂ sample after CO oxidation reaction at 325 °C. As can be seen, the size of Pt remains almost unchanged compared to the pristine 0.2Pt/Al₂O₃-300H₂ sample.

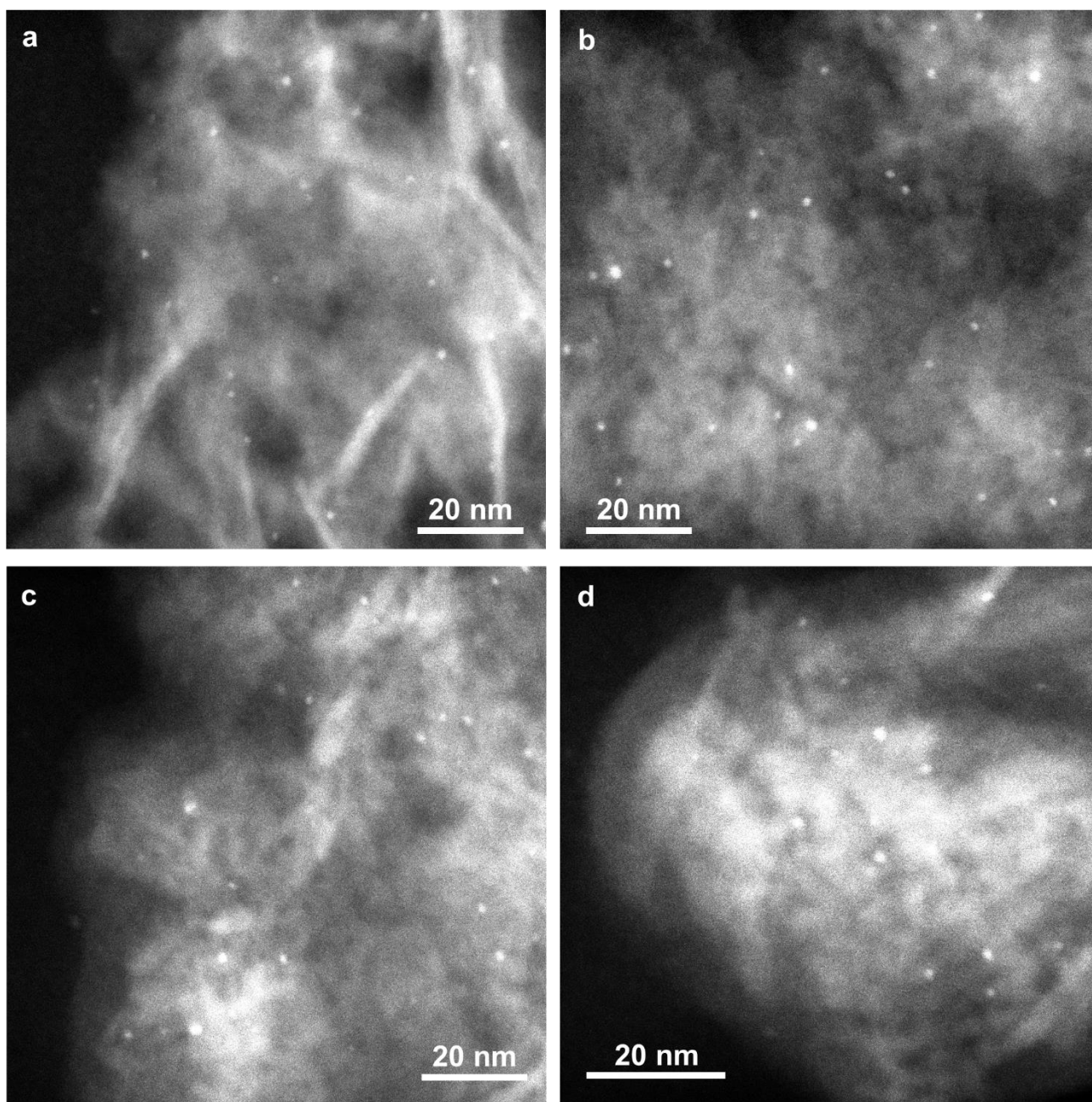


Figure S35. STEM images of 0.2Pt/Al₂O₃-450H₂ sample after CO oxidation reaction at 325 °C. As can be seen, the size of Pt remains almost unchanged compared to the pristine 0.2Pt/Al₂O₃-450H₂ sample.

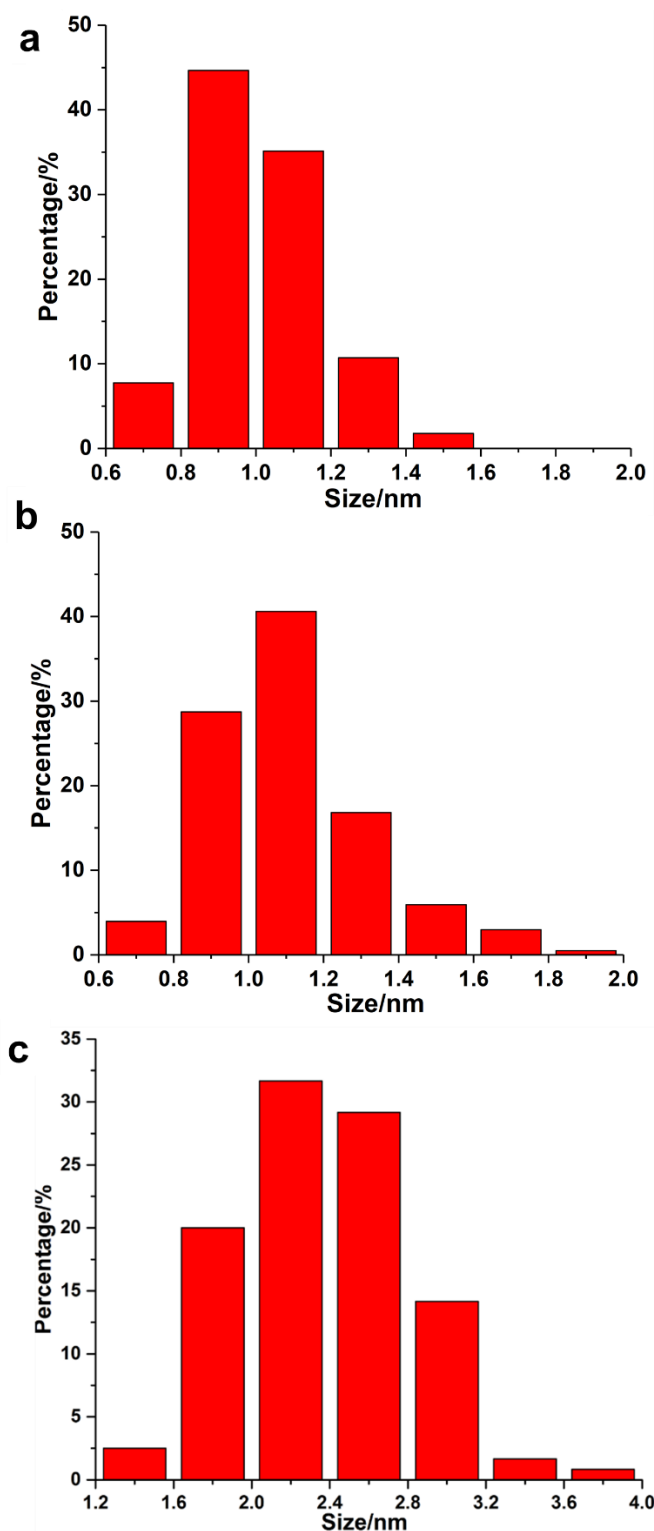


Figure S36. Particle size distribution of Pt particles in different 0.2Pt/Al₂O₃ samples after CO+O₂ reaction at 325 °C. (a) 0.2Pt/Al₂O₃-300H₂, (b) 0.2Pt/Al₂O₃-450H₂ and (c) 0.2Pt/Al₂O₃-SA. As can be seen in this figure, after CO oxidation reaction, the average size of Pt particles in 0.2Pt/Al₂O₃-300H₂ and 0.2Pt/Al₂O₃-450H₂ is around 1 nm while Pt particles present in the used 0.2Pt/Al₂O₃-SA sample are mostly larger than 2 nm.

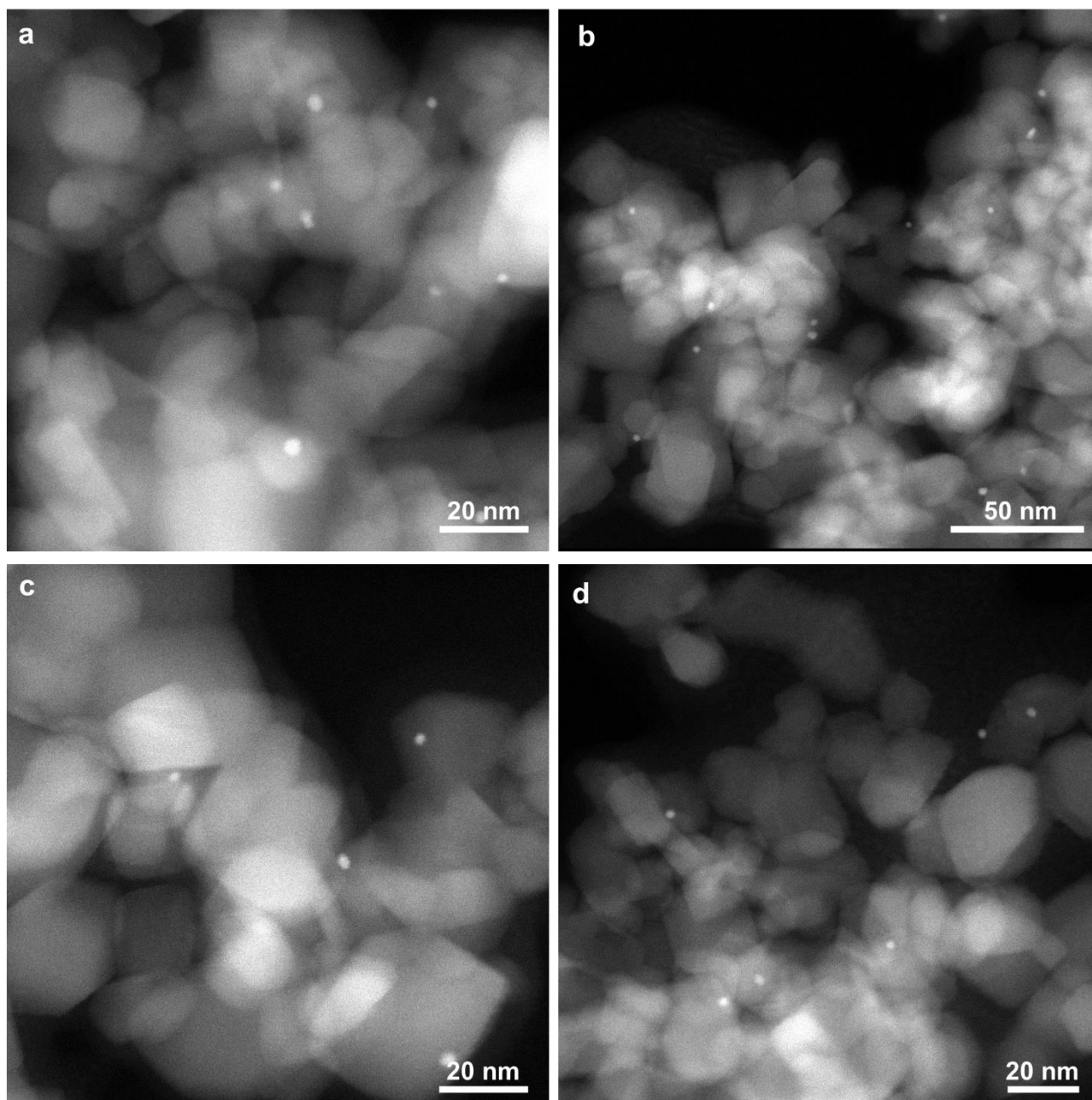


Figure S37. STEM images of 0.03Pt/TiO₂-SA after CO oxidation reaction, showing the presence of Pt nanoparticles supported on TiO₂. These images indicate that, singly dispersed Pt atoms on TiO₂ surface are not stable and they can agglomerate into nanoparticles or clusters under reaction conditions.

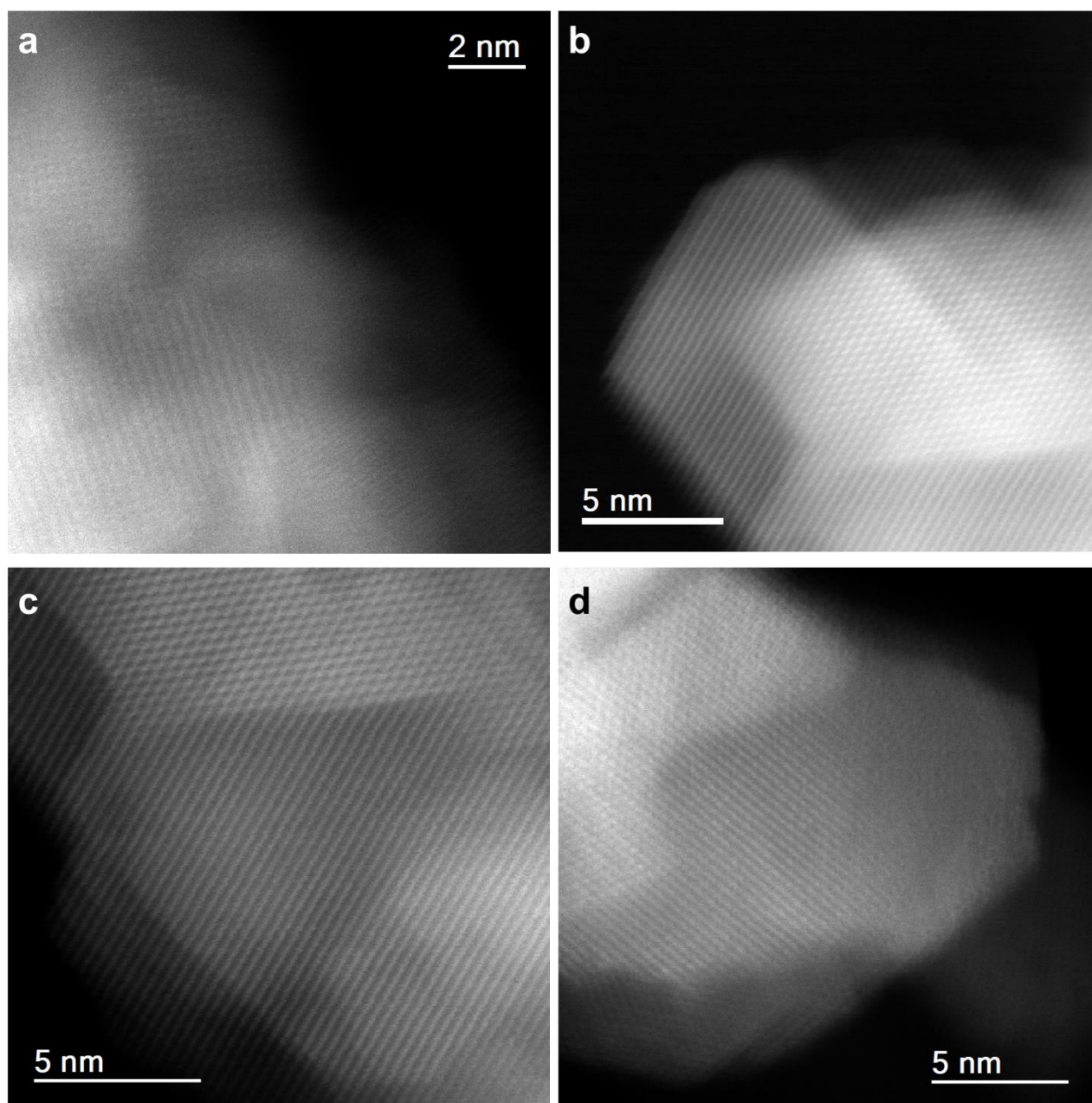


Figure S38. STEM image of as-prepared 0.2Pt/CeO₂-SA with atomically dispersed Pt species. No Pt nanoparticles can be observed in the fresh catalyst.

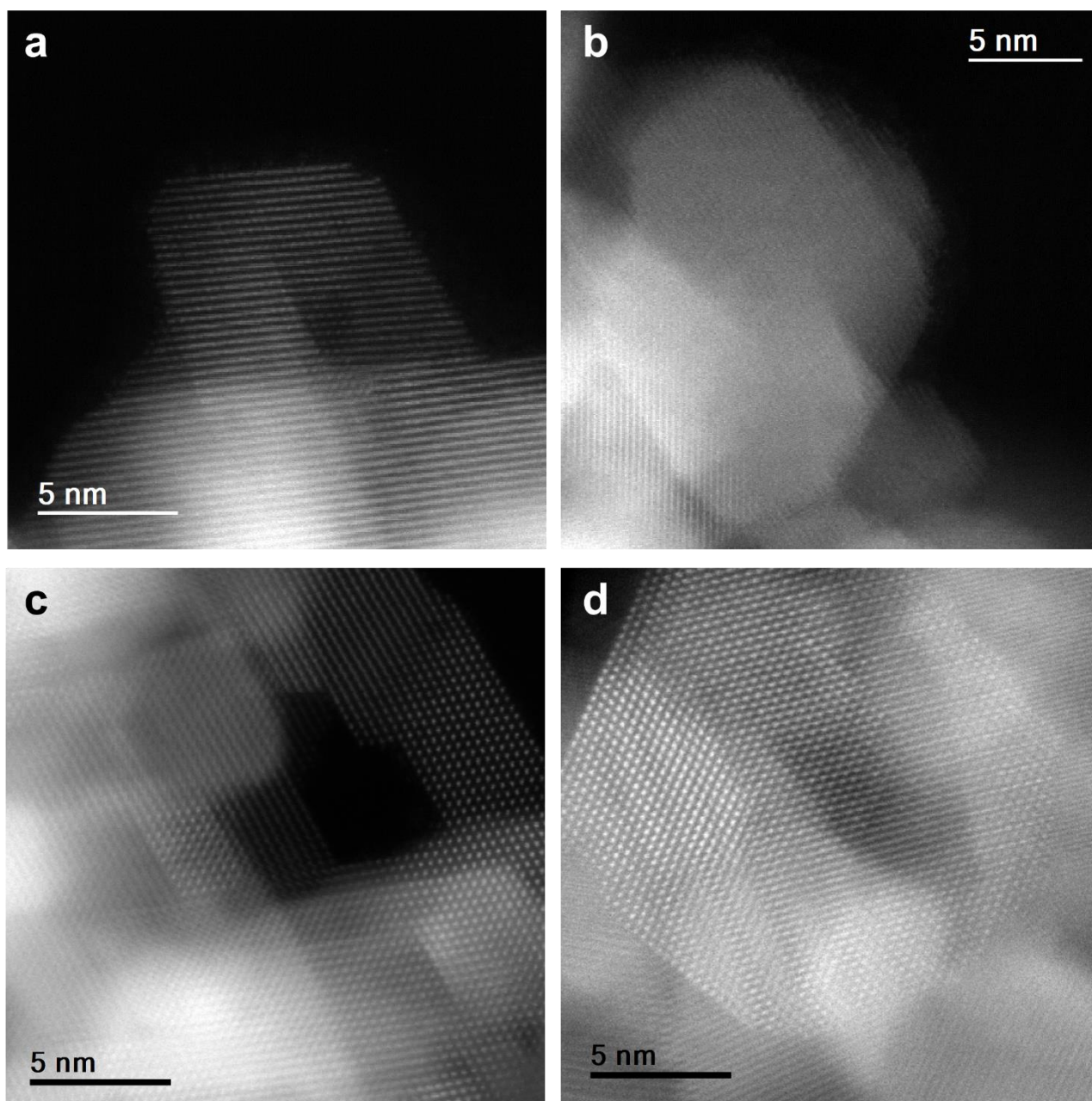


Figure S39. STEM image of 0.2Pt/CeO₂-SA after CO+O₂ reaction. No Pt nanoparticles can be observed in the fresh catalyst. Pt remains to be atomically dispersed in the used catalyst after CO+O₂ reaction, suggesting the higher stability of Pt atoms on CeO₂.

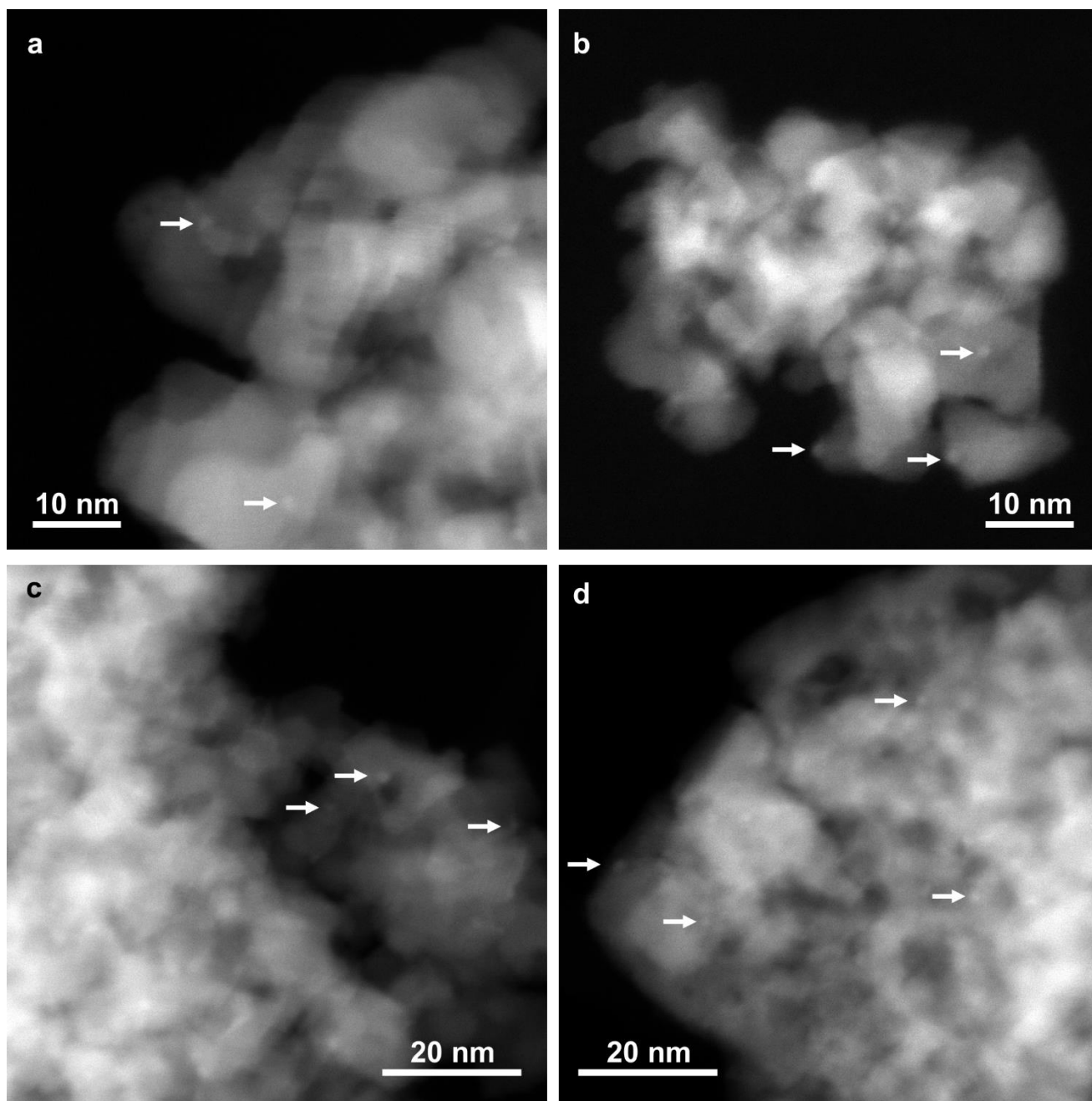


Figure S40. STEM images of 0.2Pt/CeO₂-500H₂ sample, showing the presence of Pt nanoparticles of 1-2 nm formed after reduction of the pristine 0.2Pt/CeO₂-SA sample at 500 °C by H₂.

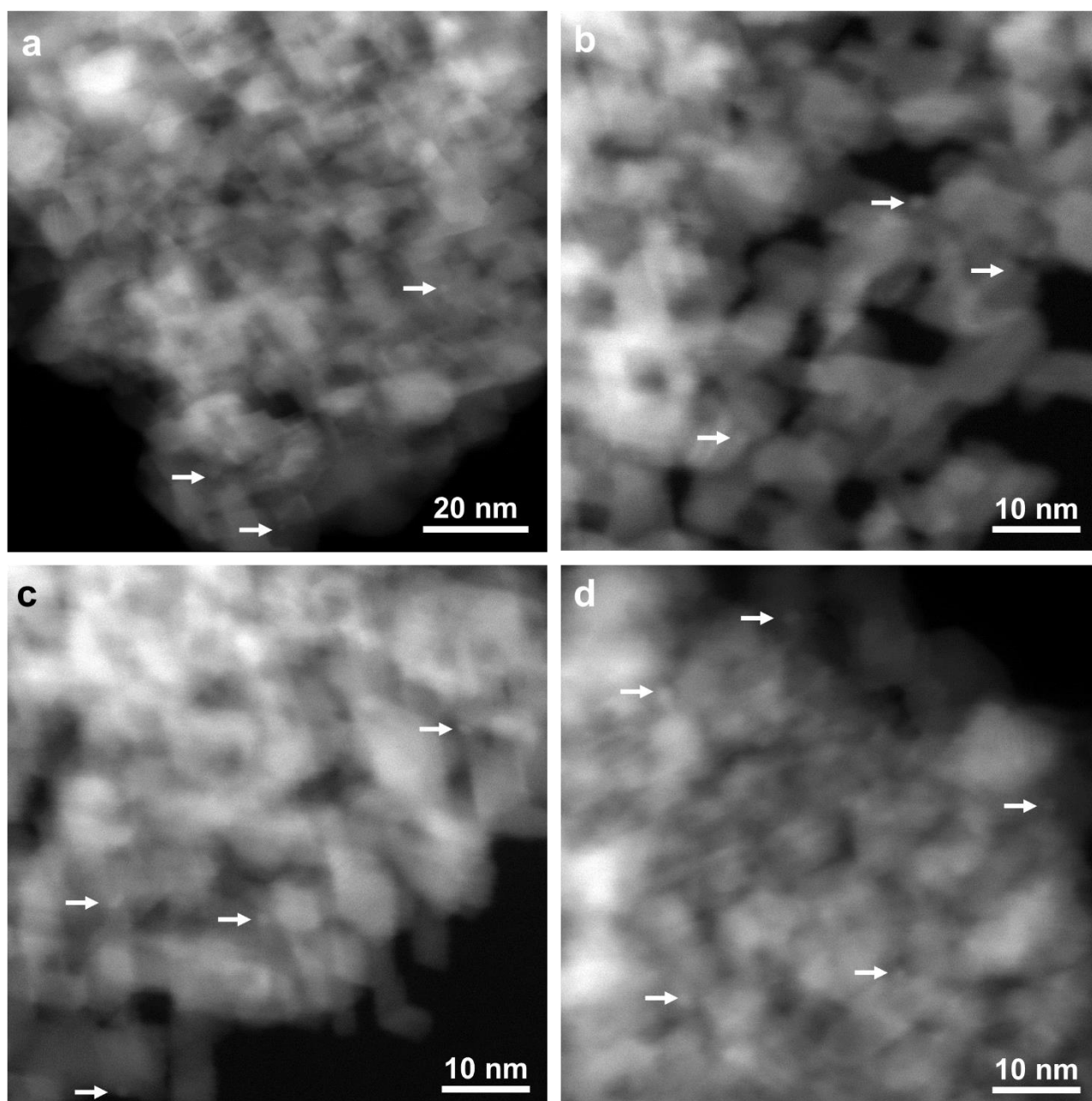


Figure S41. STEM images of 0.2Pt/CeO₂-500H₂ sample after CO+O₂ reaction. Pt nanoparticles are still present in the used catalyst.

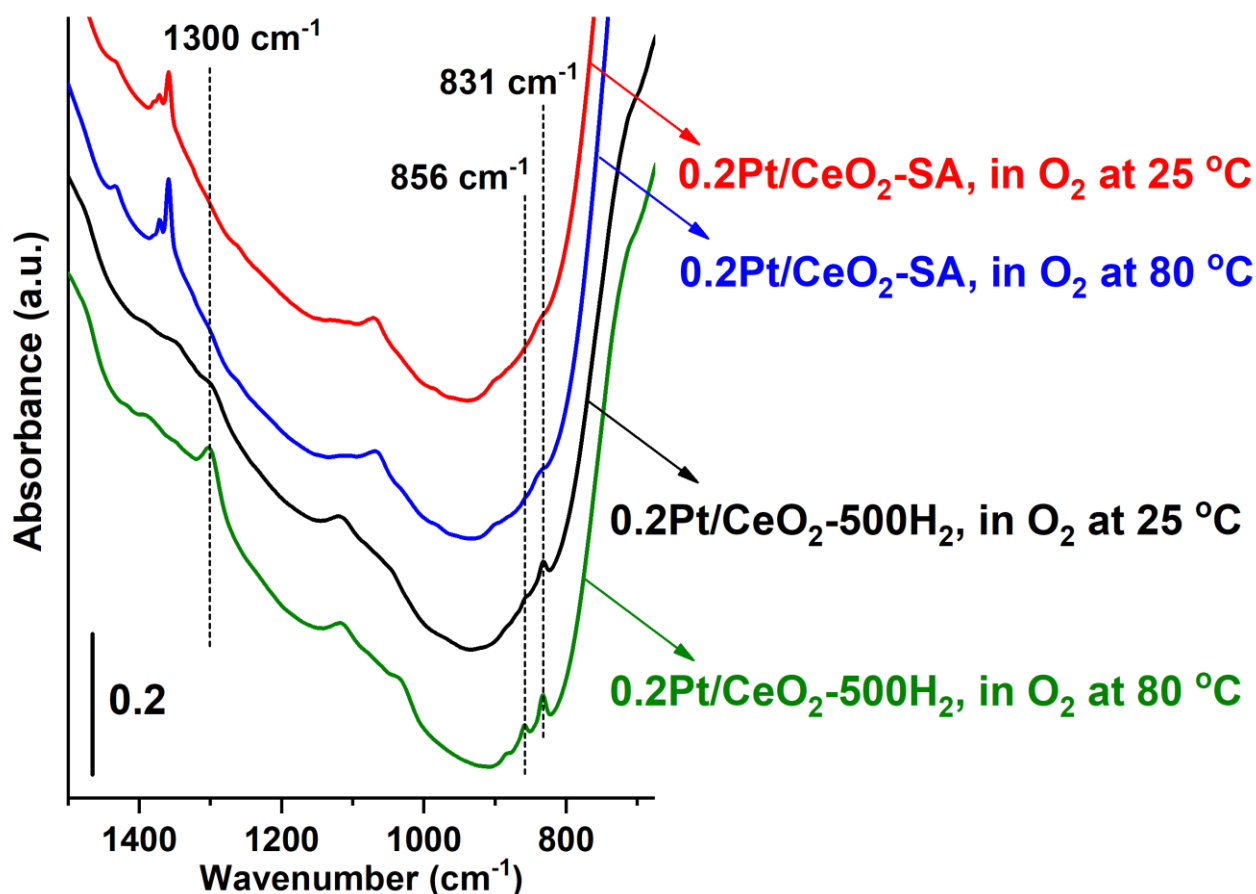


Figure S42. In situ IR spectra of 0.2Pt/CeO₂-SA containing Pt single atoms and 0.2Pt/CeO₂-500H₂ sample containing Pt nanoparticles in O₂. After the activation treatment, the sample was exposed to O₂ and then the IR spectrum was recorded in O₂ atmosphere. The absorption bands at 831, 856 and 1300 cm⁻¹ corresponding to peroxide species were only observed with the 0.2Pt/CeO₂-500H₂ sample, which can be associated to the activation of O₂ on this 0.2Pt/CeO₂ sample. However, no signal of activated oxygen species could be observed with the 0.2Pt/CeO₂-SA sample.

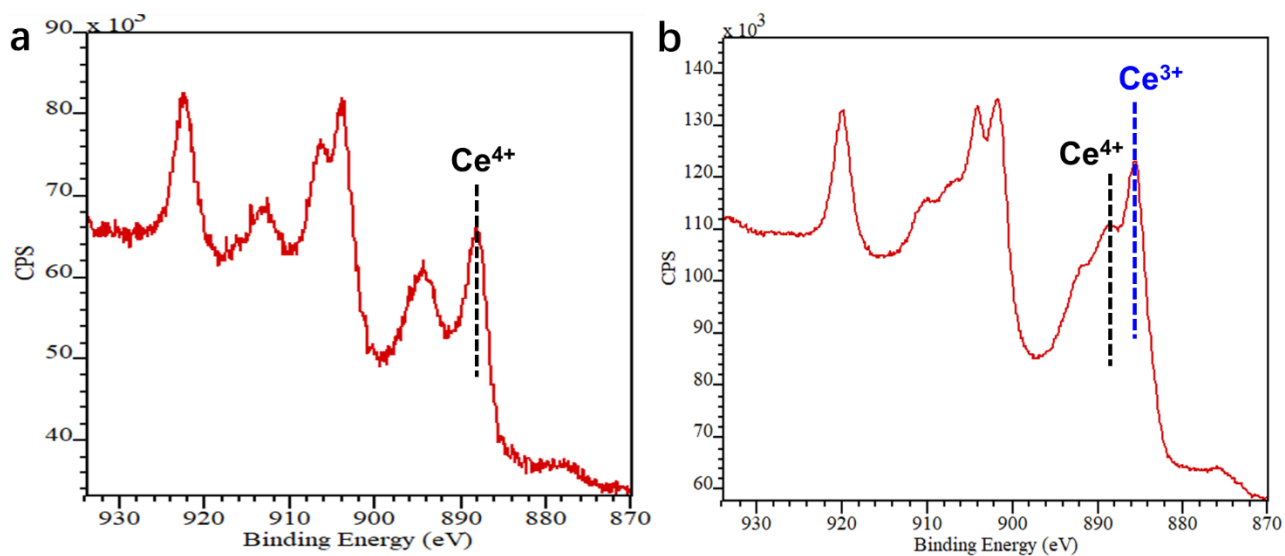


Figure S43. XPS spectra of Ce 3d region of 0.2Pt/CeO₂ samples. (c) 0.2Pt/CeO₂-SA sample and (b) 0.2Pt/CeO₂-500H₂, measured after pre-reduction by H₂.

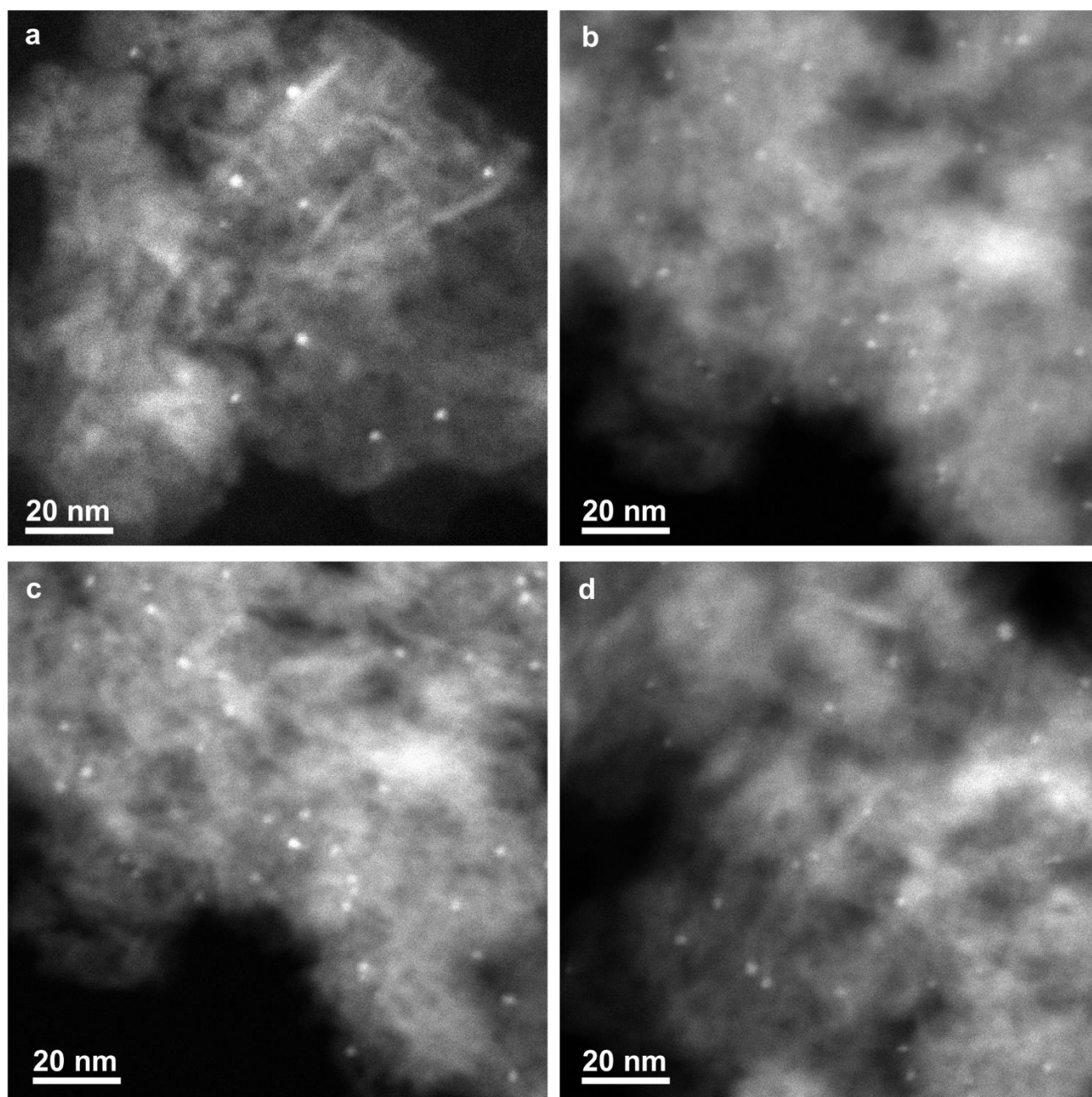


Figure S44. STEM images of 0.2Pt/Al₂O₃-SA sample after propane dehydrogenation reaction at 600 °C. As can be seen, a large number of Pt nanoparticles are formed in the used catalyst,

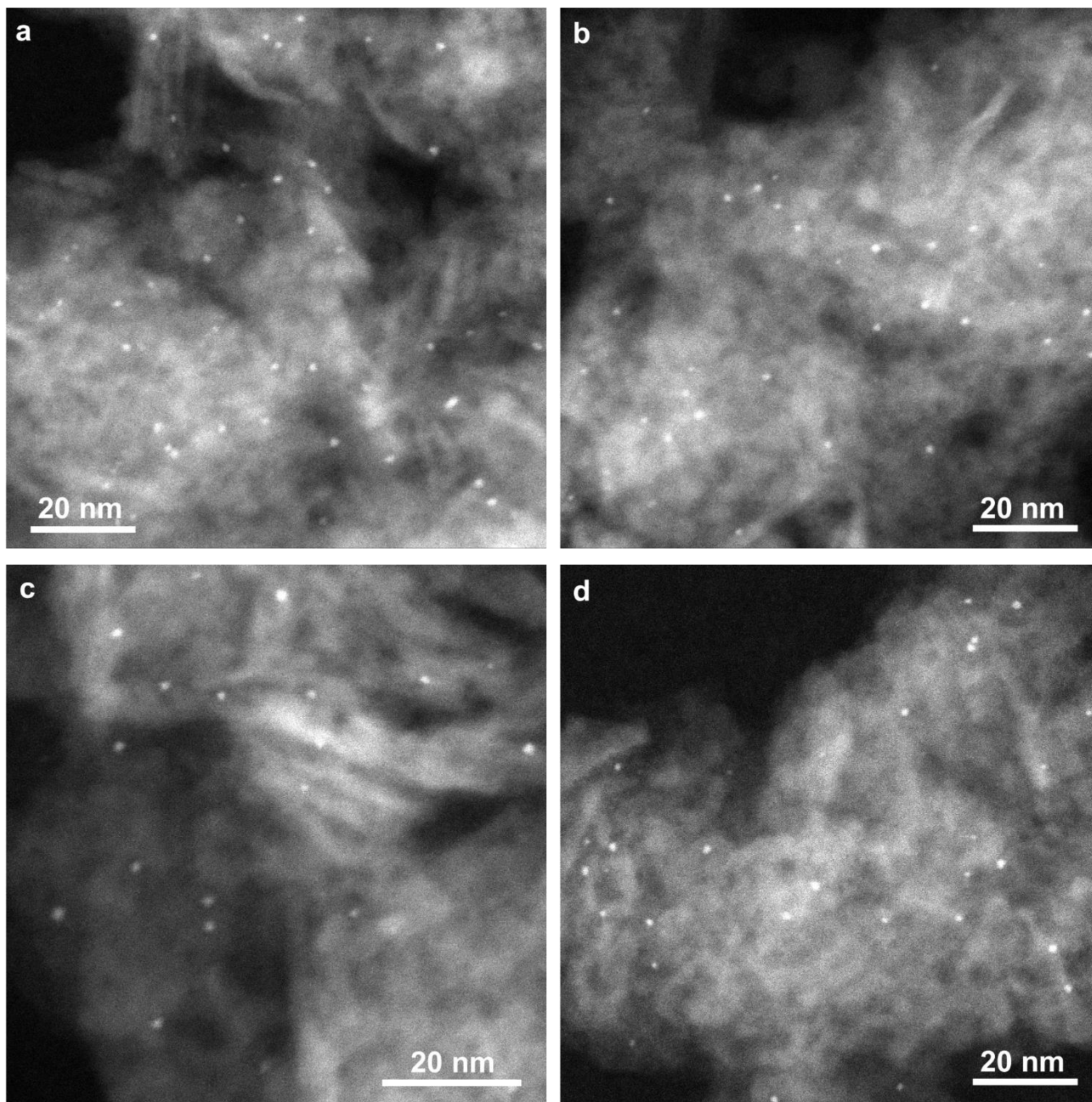


Figure S45. STEM images of 0.2Pt/Al₂O₃-200H₂ sample after propane dehydrogenation at 600 °C.

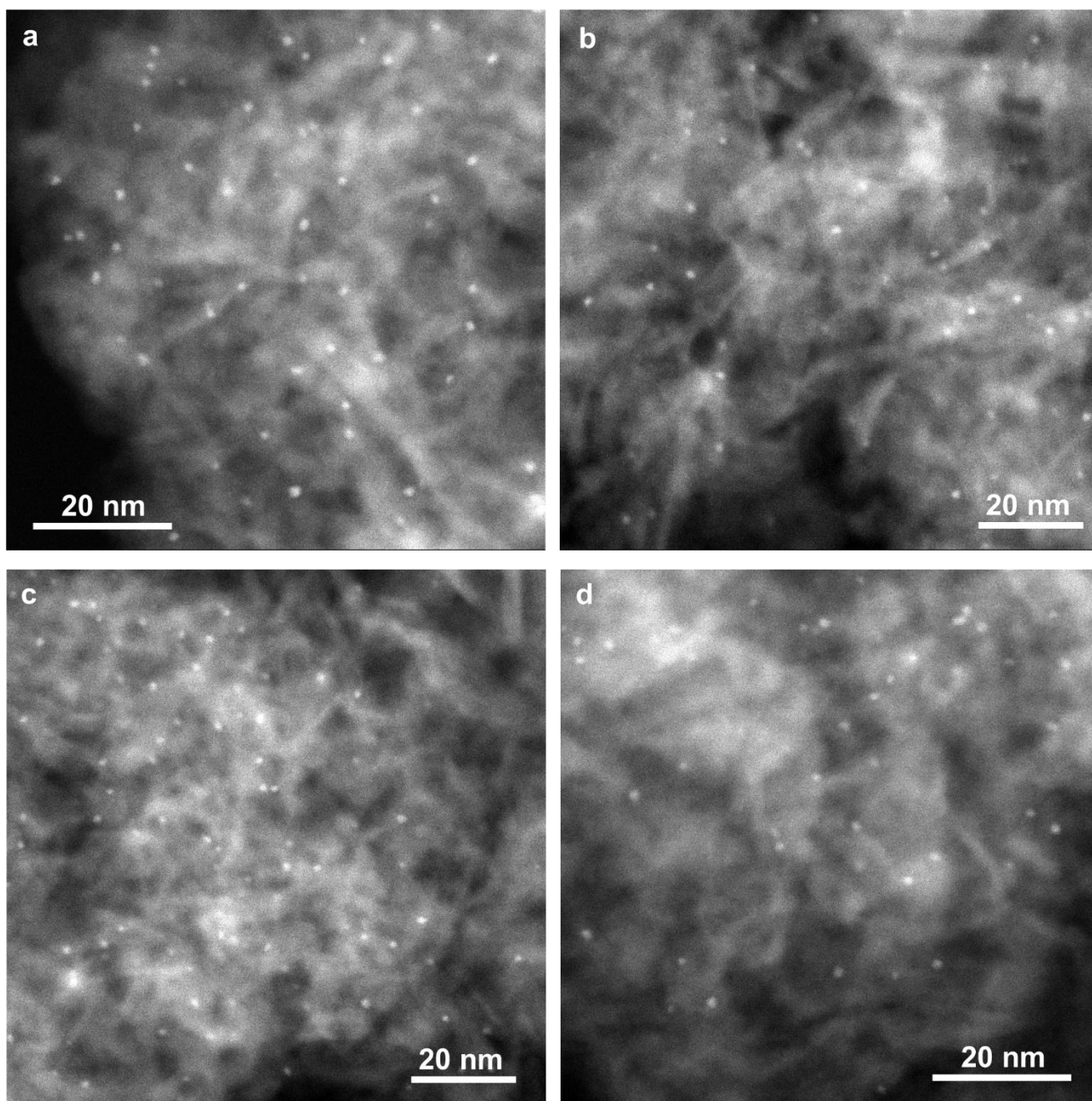


Figure S46. STEM images of 0.2Pt/Al₂O₃-450H₂ sample after propane dehydrogenation at 600 °C.

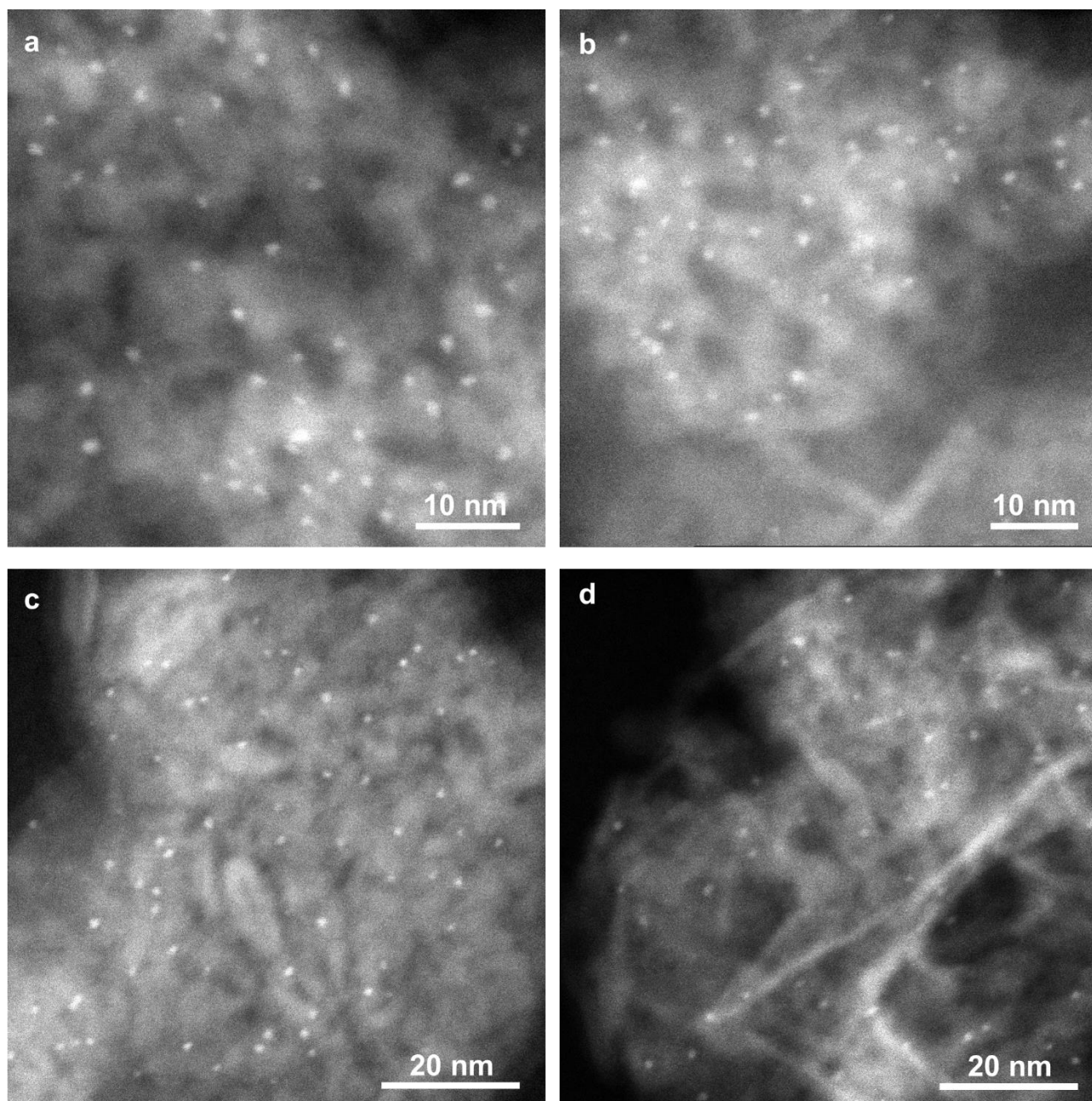


Figure S47. STEM images of the pristine 0.2Pt/Al₂O₃-600H₂ sample, prepared by reduction of Pt/Al₂O₃-SA sample at 600 °C by H₂.

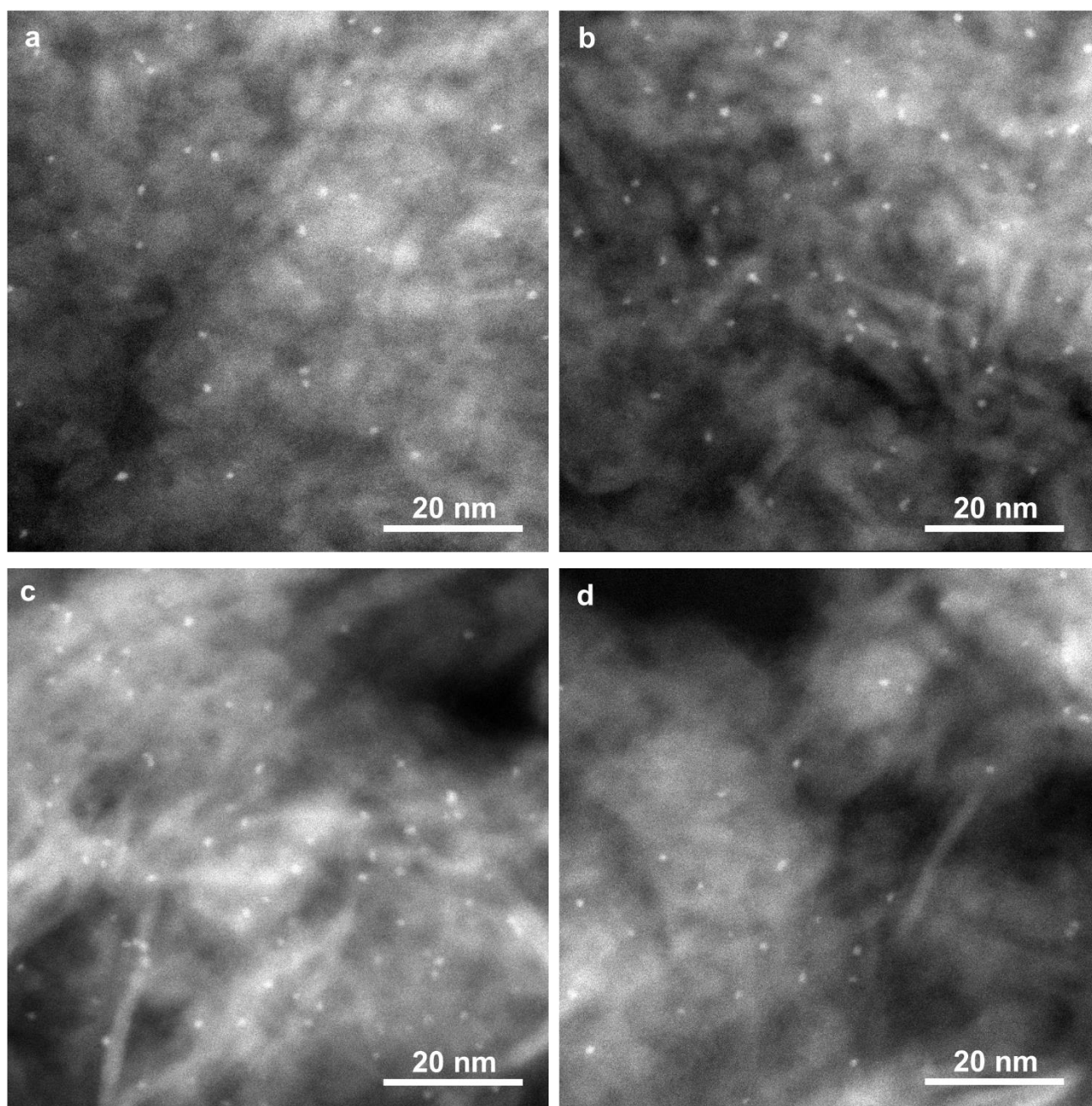


Figure S48. STEM images of 0.2Pt/Al₂O₃-600H₂ sample after propane dehydrogenation at 600 °C.